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SALTS OF GALACTURONIC ACID AND THEIR APPLICATION TO THE PREPARATION OF GALACTURONIC ACID FROM PECTIC SUBSTANCES

By Horace S. Isbell and Harriet L. Frush

ABSTRACT

Twelve new salts of galacturonic acid have been prepared and their properties investigated. Crystalline sodium, potassium, ammonium, cadmium, and silver galacturonates have been found to contain the beta pyranose modification, and crystalline calcium and strontium galacturonates, the alpha modification. A unique type of double salt containing a monovalent and a divalent metal in combination with the alpha pyranose modification of galacturonic acid has been obtained, and the following members of this class have been crystallized and studied: Sodium calcium, sodium strontium, sodium barium, sodium cadmium, sodium lead, and potassium calcium galacturonates. Mutarotation studies have been conducted in order to determine the structure of the galacturonate component in the salts. The crystallizing properties of the normal calcium and strontium galacturonates, and especially of the sodium calcium and sodium strontium galacturonates, makes these salts particularly suitable for the separation of galacturonic acid from the hydrolytic liquors of plant materials.

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I. PREPARATION OF GALACTURONIC ACID FROM PECTIC SUBSTANCES

Even though galacturonic acid in the form of pectic substances comprises a large part of the carbohydrate material of plants, its properties have not been closely studied nor has its industrial application been explored. The slowness in the development of the chemistry of galacturonic acid has undoubtedly been due to the lack of a convenient method for the separation of the acid from plant material. Heretofore [1][1] the preparation of galacturonic acid has involved, first, the preparation of pectin or pectic acid from the plant material; second, hydrolysis of the purified pectin or pectic acid; third, alcoholic precipitation of impurities; and finally, crystallization of the galacturonic acid in the form of a monohydrate from the alcoholic extract.[2] Extraction and crystallization processes involving the use of alcohol are expensive and preclude the production of a low-cost product.

Prior to the present investigation a crystalline sodium salt [8, 9], an amorphous barium [10, 11, 12] and an amorphous calcium [8, 9] salt were reported in the literature, but these compounds are not satisfactory for the separation of galacturonic acid from crude mixtures. Since a slightly soluble salt would provide a means for separating galacturonic acid directly from the hydrolyzates of plant materials, the preparation of a series of salts was undertaken with the object of obtaining a compound that could be used for separating galacturonic acid from the liquor obtained by the partial hydrolysis of such materials as apple pulp, citrus fruit pulp, and beet pulp.

The present investigation was successful in that new crystalline potassium, ammonium, cadmium, silver, calcium, and strontium salts have been obtained, and, in addition, a new type of double salt. The double salts, which appear to be unique in the field of carbohydrate chemistry, contain one atom of a monovalent metal and one of a divalent metal in combination with three galacturonate radicals. As representatives of the class of double compounds, crystalline sodium calcium, sodium strontium, sodium barium, sodium cadmium, sodium lead, and potassium calcium galacturonates have been prepared.[3] The double salts, in general, are less soluble than the normal salts and crystallize exceptionally well. For this reason they are useful for separating galacturonic acid from sirups of relatively low purity. Thus it has been found that sirups obtained by the hydrolysis of pectin-containing material, when neutralized with a calcium base yield crystalline calcium galacturonate, or when neutralized with a sodium and a calcium base yield crystalline sodium calcium galacturonate.

The existence of a simple means for obtaining galacturonates from cheap raw materials opens the way for numerous applications in the

[1] Figures in brackets indicate the literature references at the end of the paper.

[2] Early work on the preparation of galacturonic acid from pectic substances was done by Ehrlich and coworkers, who developed a method that gives high yields of galacturonic acid but requires a pectinase especially prepared from Penicillium Ehrlichii [2]. Morrell, Baur, and Link [3] described a method for preparing the acid in quantity from commercially available citrus pectic acid by means of acid hydrolysis. Mottern and Cole [4] modified the Ehrlich method by using commercially available pectic acid and a commercial pectinase, Pectinol 100D. Pigman [5] improved the procedure further by the use of methyl alcohol as a solvent for extracting the crude galacturonic acid from the hydrolyzate. Later, Isbell and Frush [6] introduced the use of acetic acid as a solvent in the crystallization of galacturonic acid, and Rietz and Maclay [7] pointed out that the modified Ehrlich method is applicable to commercial pectins.

[3] After the work described in this paper had been completed and the manuscript written, the preparation of sodium calcium galacturonate and potassium calcium galacturonate was reported in a patent [13] issued January 4, 1944, to Pasternack and Regna. Our work was conducted without knowledge of that described in the afore-mentioned patent.

chemical industry. Catalytic reduction of the calcium salt with hydrogen in the presence of Raney nickel yields calcium *L*-galactonate, an intermediate in a new process for the manufacture of vitamin C that has been developed by the senior author. Oxidation of the salts in alkaline solution with oxygen yields salts of trihydroxyglutaric acid [14], and electrolytic oxidation in the presence of bromides or oxidation with chlorous acid yields mucic acid [15]. We have observed that the sodium, potassium, and calcium salts inhibit the precipitation of the hydroxides of the amphoteric metals, such as aluminum and chromium. Hence some of the galacturonates may find use in the tanning and dyeing industries. Furthermore, the silver salt in solution decomposes spontaneously with the formation of silver mirrors; hence it might be used for the silvering of glass. The new salts are of academic interest because they are characteristic derivatives of galacturonic acid suitable for identification purposes, and because they provide a convenient raw material for the production of substances having the *L*-galactose configuration.

Directions are given on page 87 for the preparation of calcium galacturonate from citrus pectin, and on page 90 for the preparation of sodium calcium galacturonate from citrus pectic acid. The preparation of the same salts from cheaper raw materials as, for example, the pulp which remains after the extraction of sugar from sugar beets, will be the subject of a future publication.

II. MODIFICATIONS OF GALACTURONIC ACID IN CERTAIN SALTS

Inasmuch as the galacturonate radical can exist in pyranose, furanose, and open-chain modifications, salts of galacturonic acid having the same empirical formula but different structures and configurations are possible. It is therefore of interest to ascertain what modifications exist in the new salts; this may be determined by a study of the optical rotations. In a previous publication [6] it was shown that the two crystalline modifications of galacturonic acid comprise a pair of pyranoses, and that they give complex mutarotations which resemble the mutarotations of α- and β-*D*-galactose.

Measurements have now revealed that the salts of galacturonic acid also exhibit mutarotation. When the salts are dissolved in carbon-dioxide-free water, the changes in optical rotation are too rapid for accurate measurement, and the mutarotation constants vary widely for different salts and for different samples of the same salt. Somewhat more consistent results were obtained from measurements conducted in water saturated with carbon dioxide, but, nevertheless, the variation in the constants for the various salts was too large to permit a satisfactory correlation of optical rotation and structure. In every case the mutarotation of the salt was found to be more rapid than the mutarotation of the free acid.

The more rapid mutarotations of the salts appear to be caused by the catalytic effect of the galacturonate ion. As shown by Lowry [16] and by Brønsted and Guggenheim [17], the mutarotation reaction is accelerated by all substances capable of donating protons, or accepting protons. In an aqueous solution of a sugar the principal catalysts are the undissociated water molecules, hydrogen ions, and hydroxyl ions. Salts of carboxylic acids, such as sodium acetate,

accelerate mutarotation through combination of carboxylate ions with protons. The carboxylate ions derived from salts of galacturonic acid act in similar manner and thereby accelerate the mutarotation. For this reason the mutarotation constants obtained for the salts of galacturonic acid depend in part on the concentration of the salt. Solutions of galacturonic acid contain relatively small concentrations of the carboxylate ion, but the acid affects the rate of mutarotation through the catalytic effect of the hydrogen ions and of the undissociated acid molecules. In dilute aqueous solution the catalytic effect of the acid is less than the catalytic effect of the salt, and consequently the mutarotation of the acid is less rapid than that of the salt.

The correlation of the mutarotations of the salts with those of the alpha and beta modifications of galacturonic acid is complicated by these factors. However, by treating the salts with 1 equivalent of a mineral acid they are converted almost instantaneously into galacturonic acid, and the mutarotation which follows is essentially that of the free acid in the presence of a salt of a strong acid. Inasmuch as salts of strong acids have little effect on the mutarotation rate, the constants obtained for the salts in the presence of an equivalent quantity of acid should be comparable with the constants for galacturonic acid in aqueous solution of like concentration.

Some results obtained by measurement of the mutarotation which follows dissolution of 0.002 equivalent of a salt of galacturonic acid in 25 ml of water containing 0.002 equivalent of nitric acid are summarized in the form of the mutarotation equations reported in table 1.

TABLE 1.—*Optical rotations of salts dissolved in an equivalent quantity of aqueous nitric acid* [a]

Substance	Mutarotation equation [b]	Initial rotation [c]
	ALPHA PYRANOSE MODIFICATIONS	
		°S
α-D-Galacturonic acid [d]	$°S=+9.52\times10^{-0.0119t}+2.08\times10^{-0.115t}+10.01$	+21.61
Calcium galacturonate	$°S=+9.39\times10^{-0.0144t}+2.25\times10^{-0.105t}+9.93$	+21.57
Strontium galacturonate	$°S=+9.26\times10^{-0.0153t}+2.41\times10^{-0.114t}+10.03$	+21.70
Sodium calcium galacturonate	$°S=+9.31\times10^{-0.0137t}+2.52\times10^{-0.123t}+10.02$	+21.85
Sodium strontium galacturonate	$°S=+9.25\times10^{-0.0149t}+1.89\times10^{-0.143t}+9.92$	+21.06
Sodium barium galacturonate	$°S=+8.63\times10^{-0.0147t}+2.01\times10^{-0.112t}+9.78$	+20.42
Sodium cadmium galacturonate	$°S=+8.69\times10^{-0.0148t}+1.99\times10^{-0.104t}+9.87$	+20.55
Sodium lead galacturonate	$°S=+9.54\times10^{-0.0480t}+1.68\times10^{-0.263t}+10.01$	+21.23
Potassium calcium galacturonate	$°S=+9.52\times10^{-0.0154t}+2.04\times10^{-0.126t}+9.91$	+21.47
	BETA PYRANOSE MODIFICATIONS	
β-D-Galacturonic acid [d]	$°S=-5.81\times10^{-0.0120t}+0.93\times10^{-0.092t}+9.71$	+4.83
Sodium galacturonate	$°S=-7.19\times10^{-0.0110t}+1.35\times10^{-0.107t}+9.74$	+3.90
Potassium galacturonate	$°S=-7.09\times10^{-0.0134t}+1.12\times10^{-0.129t}+9.91$	+3.94
Ammonium galacturonate	$°S=-7.49\times10^{-0.0124t}+0.80\times10^{-0.108t}+9.99$	+3.30
Cadmium galacturonate	$°S=-6.37\times10^{-0.0142t}+1.09\times10^{-0.111t}+9.90$	+4.62

[a] 0.002 equivalent of the salt dissolved in 25 ml of water containing 0.002 equivalent of nitric acid and read in a 4-dm tube with a Bates saccharimeter. The volume after addition of the salt was 25.2 ml. The optical rotation is essentially that of the acid liberated from the salt.

$[\alpha]_D^{20}={}°S\times5.62$ (based on the weight of anhydrous galacturonic acid).

$[\alpha]_D^{20}=\dfrac{°S\times0.3462\times25.2}{4\times0.002\times\text{equivalent wt of the salt}}$ (based on the weight of the salt).

[b] The equations were calculated by the method described on page 156 of [18].

[c] The initial rotation is the calculated value of °S when $t=0$.

[d] 0.002 equivalent of the acid dissolved in 25 ml of water rather than in dilute nitric acid.

Equations for the mutarotations of α- and β-*D*-galacturonic acid, also given in table 1, were obtained by use of solutions containing 0.002 equivalent dissolved in 25 ml of water. The initial rotations at the right of the table are expressed in sugar degrees; multiplication by the factor 5.62 converts these values to specific rotation in terms of anhydrous galacturonic acid in the solution.

Inspection of the results reveals that the initial rotation of the acid set free from the calcium, strontium, sodium calcium, sodium strontium, sodium barium, sodium cadmium, sodium lead, and potassium calcium salts is in agreement with the initial rotation of α-*D*-galacturonic acid monohydrate, and that the initial rotation of the acid set free from the sodium, potassium, ammonium, and cadmium salts is in approximate agreement with the initial rotation of β-*D*-galacturonic acid. This is evidence that the salts in the first-mentioned group contain the alpha pyranose modification of galacturonic acid and that the salts in the second group contain the beta pyranose modification.[4]

This classification is supported further by the character of the changes in optical rotation which take place after dissolution of the salts. The change during the early part of the mutarotation of the first group of salts is more rapid than that during the later stages, and the mutarotation follows an equation of the type:

$$[\alpha]_t = A \times 10^{-m_1 t} + B \times 10^{-m_2 t} + C.$$

The net change during the early part of the mutarotation of the second group of salts is slow, and the mutarotation follows an equation of the type:

$$[\alpha]_t = -A' \times 10^{-m_1 t} + B' \times 10^{-m_2 t} + C.$$

The complex mutarotations of the first group are like the mutarotations characteristic of substances having the *α-galacto*-pyranose structure, whereas those of the second group are like the mutarotations characteristic of substances having the *β-galacto*-pyranose structure.

III. PREPARATION AND PROPERTIES OF SALTS OF GALACTURONIC ACID

1. SODIUM GALACTURONATE, $NaC_6H_9O_7$

This salt was prepared by neutralization of a 20-percent aqueous solution of galacturonic acid with sodium bicarbonate, followed by the addition of ethyl alcohol to the point of saturation. The crystals so obtained appear to differ from those described by Ehrlich and Schubert [8] in that they exhibit mutarotation and can be recrystallized from water. Ono [9] described a sodium salt crystallizable from water but failed to note any mutarotation. The material used in the present investigation was recrystallized from water by the addition of alcohol, and dried in a vacuum desiccator at room temperature over calcium chloride. Substantially quantitative yields were obtained.

Analysis: Calculated for $NaC_6H_9O_7$: C, 33.5; H, 4.2. Found: C, 33.5; H, 4.3.

[4] Measurements were not made on the silver salt in the presence of nitric acid, but since the mutarotation in water is like that of salts having the beta pyranose structure, the silver salt is classified as a beta pyranose.

According to our measurements, in 4-percent aqueous solution, sodium galacturonate shows an initial specific rotation of +11.5°, an equilibrium rotation of +36.0°, and the mutarotation recorded in table 2. Previously, Ehrlich and Schubert [8] reported $[\alpha]_D^{22}=+36.02°$ without mutarotation, and Ono [9] reported $[\alpha]_D^{20}=+38°$, likewise without mutarotation. The initial and equilibrium rotations (+11.5° and +36.0°) of the salt dissolved in water are considerably lower than the initial and equilibrium rotations of the salt dissolved in an equivalent quantity of aqueous nitric acid (+19.7° and +49.2°). Similar differences have been found for other salts, and may be ascribed to the presence on carbon 5 of a carboxylate group in the water solutions and of a carboxyl group in the acid solutions.

The mutarotation of the salt (table 2) resembles the mutarotation of *β-D-galacto*-pyranose and other substances having the *β-D-galacto*-pyranose structure. The character of the changes shows that the sodium salt in aqueous solution establishes an equilibrium state involving at least three modifications. These must include the alpha and beta pyranose modifications and a furanose modification for the following reasons:

(a) The substance crystallizes in the beta pyranose form.

(b) Upon addition of a calcium salt, a sodium calcium salt of galacturonic acid containing the alpha pyranose modification crystallizes from solution.

(c) The existence of a furanose modification in solution was shown by our previous observation [6] that a solution of sodium galacturonate on oxidation with bromine water gives rise to the optically active gamma and delta lactones of mucic acid. Presumably the gamma and delta lactones of mucic acid are formed directly from the furanose and pyranose modifications respectively.

The lactones of mucic acid just mentioned are obtained by oxidation of galacturonic acid and should not be confused with lactones of galacturonic acid formed by condensation of the carboxyl with the hydroxyl of carbon 2 or carbon 3. In dilute aqueous solutions of galacturonic acid, the concentrations of lactones are low, and their presence does not materially affect the optical rotations. Lactone formation does not occur in solutions of salts of galacturonic acid.

The mutarotation observed after dissolution of the sodium salt in nitric acid (table 3) resembles the mutarotation of *β-D*-galacturonic acid (table 4) at the same molecular concentration, but there are certain differences which indicate that the two samples were not of like purity. The sample of sodium galacturonate, when dissolved in an equivalent quantity of nitric acid, showed an initial rotation of +3.90° *S*, a rapid mutarotation involving a change of 1.35° *S*, and a slow mutarotation involving a change of 7.19° *S*. The sample of galacturonic acid reported in table 4 showed an initial rotation of +4.83° *S*, a rapid mutarotation reaction involving a change of 0.93° *S*, and a slow mutarotation reaction involving a change of 5.81° *S*. Other samples of *β-D*-galacturonic acid prepared by crystallization from both acetic acid and alcohol gave mutarotations which varied over a considerable range. It would therefore appear that the sample of *β-D*-galacturonic acid was not entirely free from the alpha modification, but unfortunately we have not been able to obtain a sample of galacturonic acid that has a lower initial rotation than that reported

here.[5] The initial specific rotation of the acid set free from sodium galacturonate is +21.9°, whereas for crystalline *β-D*-galacturonic acid Ehrlich and Schubert reported +27° [8], and we found +31.1° [6]. Since it is difficult to obtain the beta modification free from traces of the alpha, it is believed that the acid set free from the salt is more

TABLE 2.—*Mutarotation of sodium galacturonate in water saturated with carbon dioxide* [a]

4.0 g of $NaC_6H_9O_7$ per 100 ml at 20° C, read in a 4-dm tube with a Bates saccharimeter.

$°S = -14.63\times10^{-0.0197t} + 3.45\times10^{-0.123t} + 16.42$.

$[\alpha]_D^{20} = °S \times 2.19$.

$[\alpha]_D^{20} = +11.5°$ initially, +36.0° at equilibrium.[b]

Time	Observed reading	k_1+k_2	m_1	Deviation	m_2
Minutes	°S				
1.9	+4.96			1.96	
3.1	+5.09	0.0041		1.38	0.127
5.7	+5.77	.0084		0.65	.126
10.5	+7.47	.0125		.14	.133
13.5	+8.55	.0141		.06	.131
16.6	+9.53	.0150			
22.8	+11.21	.0164	0.0196		
30.4	+12.72	.0172	.0196		
40.9	+14.14	.0180	.0198		
∞	+16.42				
Average			0.0197		0.129

[a] Mutarotation constants calculated by the method described on page 156 of [18].
[b] The equilibrium value was carefully determined on a separate sample. The factor 2.19 is the ratio of the equilibrium specific rotation to the observed equilibrium rotation in °S, or 36.0÷16.42.

TABLE 3.—*Mutarotation of sodium galacturonate dissolved in an equivalent quantity of aqueous nitric acid* [a]

0.002 equivalent of $NaC_6H_9O_7$ dissolved in 25 ml of 0.08 *N* aqueous nitric acid at 20° C, and read in a 4-dm tube. pH=2.4.

$°S = -7.19\times10^{-0.0110t} + 1.35\times10^{-0.197t} + 9.74$.

$[\alpha]_D^{20} = °S \times 5.62$ (based on weight of anhydrous galacturonic acid).

Time	Observed reading	m_1	Deviation	m_2
Minutes	°S			
2.6	+3.72		0.71	
3.7	+3.72		.52	0.123
4.8	+3.80		.42	.104
6.9	+3.98		.27	.098
8.8	+4.13		.14	.114
10.8	+4.39		.12	.094
16.1	+4.96			
19.7	+5.37	0.0108		
23.6	+5.80	.0112		
28.3	+6.23	.0110		
33.0	+6.64	.0111		
37.8	+6.99	.0111		
∞	+9.74			
Average		0.0110		0.107

[a] The values of m_1 and m_2 were calculated by the method described on page 156 of [18].

[5] In this connection, it might be mentioned that the optical rotations of the crystalline modifications of galactose and arabinose also show wide variation, according to the manner in which the sugar is crystallized [19]

nearly a pure beta pyranose modification than any crystalline acid so far obtained. In view of the comparisons cited above, our crystalline sodium galacturonate is considered to be sodium *β-D*-galacturonate (sodium *β-D-galacto*-aldopentopyranose 5-carboxylate).

TABLE 4.—*Mutarotation of β-D-galacturonic acid in water saturated with carbon dioxide*

0.002 equivalent of *β-D*-galacturonic acid dissolved in 25 ml of water at 20° C, and read in a 4-dm tube. pH=2.4.

$°S = -5.81 \times 10^{-0.0120t} + 0.93 \times 10^{-0.092t} + 9.71.$

$[\alpha]_D^{20} = °S \times 5.62.$

Time	Observed reading	m_1	Deviation	m_s
Minutes	°S			
1.9	+4.82		0.62	
3.8	+4.91		.43	0.084
5.1	+4.95		.28	.108
7.0	+5.15		.23	.084
8.9	+5.31		.14	.092
17.2	+6.11			
21.2	+6.49	0.0124		
24.9	+6.78	.0118		
30.1	+7.20	.0122		
39.2	+7.74	.0120		
53.6	+8.36	.0117		
70.1	+8.87	.0120		
∞	+9.71			
Average		0.0120		0.092

2. POTASSIUM GALACTURONATE, $(KC_6H_9O_7)_2.H_2O$

This salt was prepared by neutralization of an aqueous solution of galacturonic acid with an equivalent quantity of potassium carbonate. Crystallization was effected by adding methyl alcohol to the point of turbidity and allowing the solution to stand in a closed container. Additional methyl alcohol was added from time to time as crystallization proceeded. The crystals were separated and recrystallized from aqueous methyl alcohol and dried in a vacuum desiccator at room temperature over calcium chloride. The salt is more soluble in water than the sodium salt and crystallizes more slowly.

Analysis: Calculated for $K_2C_{12}H_{20}O_{15}$: C, 29.9; H, 4.2. Found: C, 29.7; H, 4.3.

In 4-percent aqueous solution, the salt shows a specific rotation of +9.4°, (1.5 minutes after dissolution) +31.6° at equilibrium, and a complex mutarotation. The mutarotation which takes place when the salt is dissolved in an equivalent quantity of dilute nitric acid (equation given in table 1) resembles the mutarotation of *β-D*-galacturonic acid in water. The initial rotation and the course of the mutarotation show that the compound contains the beta pyranose modification and may be named potassium *β-D*-galacturonate, (potassium *β-D-galacto*-aldopentopyranose-5-carboxylate).

3. AMMONIUM GALACTURONATE, $(NH_4C_6H_9O_7)_2.H_2O$

A solution containing 5 g of galacturonic acid was neutralized with aqueous ammonium hydroxide, and the volume was adjusted to about 25 ml. Methyl alcohol was then added to saturation. The solution

was kept in a closed container for 2 days, and more alcohol was added as crystallization progressed. The crystals were separated, recrystallized from aqueous methyl alcohol, and, for analysis, dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $C_{12}H_{28}O_{15}N_2$: C, 32.7; H, 6.4. Found: C, 32.5; H, 6.5.

In 4-percent aqueous solution, the salt shows a specific rotation of +10.2° (1.7 minutes after dissolution), an equilibrium rotation of +35.5°, and a complex mutarotation. The mutarotation in water is more rapid than that of either the sodium or the potassium salt. This fact may be explained by the catalytic effect of the ammonium ion. The mutarotation which takes place when the salt is dissolved in an equivalent quantity of dilute nitric acid (equation given in table 1) is slightly faster but resembles the mutarotation of *β-D*-galacturonic acid in water. Hence the compound contains the beta pyranose modification and may be designated ammonium *β-D*-galacturonate, (ammonium *β-D-galacto*-aldopentopyranose-5-carboxylate).

4. CADMIUM GALACTURONATE $Cd(C_6H_9O_7)_2.2H_2O$

By mixing equivalent quantities of cadmium hydroxide and galacturonic acid in water a solution was obtained, which, on evaporation, gave crystalline cadmium galacturonate. The new salt crystallizes well, but it does not seem to be as characteristic of galacturonic acid as cadmium galactonate is of galactonic acid. It is considerably more soluble than the calcium salt and crystallizes more slowly. The material was recrystallized from aqueous ethyl alcohol and dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $CdC_{62}H_{22}O_{16}$: C, 27.0; H, 4.1. Found: C, 26.9; H, 4.2.

In 1.4-percent aqueous solution, the salt shows a specific rotation of +13.9° (1.9 minutes after dissolution), and an equilibrium rotation of +28.4°. The mutarotation which takes place in water containing carbon dioxide is like that found for the alkali metal salts but is considerably more rapid. The mutarotation in nitric acid (equation given in table 1) resembles the mutarotation of *β-D*-galacturonic acid closely. Hence the salt contains the beta pyranose modification, and may be designated cadmium *β-D*-galacturonate.

5. SILVER GALACTURONATE, $(AgC_6H_9O_7)_2.H_2O$

Five grams of galacturonic acid monohydrate was dissolved in 5 ml of water and treated with an excess of freshly prepared silver carbonate. The mixture was allowed to stand for 15 minutes, filtered with the aid of a small quantity of decolorizing carbon, and the filtrate was placed in the refrigerator over-night. The crystals were separated, washed with ice water, and dried over calcium chloride at room temperature in a vacuum desiccator protected from light. The crystals are colorless platelets, which are sensitive to light and decompose in the course of several weeks.

Analysis: Calculated for $Ag_2C_{12}H_{20}O_{15}$: Ag, 34.8; C, 23.3; H, 3.3. Found: Ag, 34.7; C, 23.2; H, 3.3.

The sample used for the mutarotation measurements was crystallized from water in the absence of light, filtered, and used immediately without drying. The amount of salt in solution was calculated from

the silver content. In 3.2-percent aqueous solution, the salt shows a specific rotation of +18.2° (3.6 minutes after dissolution), an equilibrium rotation of +25.1°, and a complex mutarotation similar to that of β-*D*-galacturonic acid. The initial rotation and the mutarotation indicate that the salt contains the beta pyranose modification.

6. CALCIUM GALACTURONATE $Ca(C_6H_9O_7)_2.H_2O$

(a) PREPARATION FROM GALACTURONIC ACID

Prior attempts to obtain a crystalline calcium galacturonate have been unsuccessful [9]. The difficulty in crystallizing salts of galacturonic acid may be ascribed at least in part to the existence in solution of the two pyranose modifications in dynamic equilibrium. We found that the sodium, potassium, ammonium, cadmium, and silver salts crystallize in the beta pyranose modification but were unable to obtain a similar calcium salt. However, a crystalline calcium salt of the alpha pyranose modification was obtained by adding a small quantity of water to a mixture of powdered calcium carbonate and α-*D*-galacturonic acid monohydrate in equivalent quantities. The mixture was rubbed with a glass rod and allowed to stand until crystallization took place. This material was used as seed for nucleation of calcium galacturonate sirups.

The sample used for analyatical and optical rotation measurements was prepared by treating pure galacturonic acid in 10-percent aqueous solution with an excess of calcium carbonate, filtering the solution, and seeding with crystalline calcium galacturonate. When satisfactory crystallization had taken place, the crystals were separated, and the compound was recrystallized several times from hot water. It was finally dried in a vacuum desiccator over calcium chloride at room temperature.

Analysis: Calculated for $CaC_{12}H_{20}O_{15}$: Ca, 9.0; C, 32.4; H, 4.5. Found: Ca, 9.2; C, 32.2; H, 4.6.

TABLE 5.—*Mutarotation of calcium galacturonate in water saturated with carbon dioxide*

2.0 g of $Ca(C_6H_9O_7)_2.H_2O$ per 100 ml at 20° C, read in a 4-dm tube.

$[\alpha]_D^{20} = °S \times 5.57$

Time	Observed reading	k_1+k_2 [a]
Minutes	° *S*	
3.9	+13.47	-------
4.5	+12.74	0.081
5.0	+12.23	.079
6.3	+11.35	.067
7.6	+10.37	.071
9.0	+9.64	.070
10.4	+9.11	.067
12.4	+8.46	.067
15.3	+7.85	.065
18.4	+7.43	.064
22.3	+7.08	.063
26.3	+6.90	.061
31.1	+6.75	.062
∞	+6.61	-------

[a] The decrease in the value of k_1+k_2 shows that the mutarotation is complex. The rapid reaction was nearly complete at the time of the first reading.

At room temperature, calcium galacturonate crystallizes in the form of microscopic prisms, which build aggregates occluding considerable mother liquor; at slightly higher temperatures larger cyrstals separate and the massecuite is granular. Hence it is advantageous to effect the crystallization at slightly elevated temperatures. This can be accomplished readily in a distillation flask, or in a vacuum pan, held at about 40° C. The salt is soluble in about 10 parts of boiling water and crystallizes when the hot solution is cooled. At 20° C a saturated solution contains approximately 4.9 g of calcium galacturonate monohydrate per 100 ml. The salt is not appreciably soluble in alcohol or other organic solvents. Hence, crystallization can be conveniently effected by the addition of ethyl alcohol to an aqueous solution to the point of saturation, and the crystals can be washed, to advantage, with water containing about 15 percent of alcohol.

TABLE 6.—*Mutarotation of calcium galacturonate dissolved in an equivalent quantity of aqueous nitric acid*

0.002 equivalent of $Ca(C_6H_9O_7)_2.H_2O$ dissolved in 25 ml of 0.08 *N* aqueous nitric acid at 20° C, and read in a 4-dm tube. pH = 2.2

$°S = +9.39 \times 10^{-0.0144t} + 2.25 \times 10^{-0.105t} + 9.93$

$[\alpha]_D^{20} = °S \times 5.62$ (based on weight of anhydrous galacturonic acid)

Time	Observed reading	m_1	Deviation	m_2
Minutes	°*S*			
2.3	+19.92		1.29	
3.1	+19.50		1.10	0.087
4.6	+18.70		0.71	.113
5.9	+18.21		.56	.101
7.3	+17.71		.41	.100
9.7	+16.96		.22	.122
14.9	+15.66			
20.0	+14.76	0.0146		
25.6	+13.93	.0146		
31.0	+13.30	.0143		
37.1	+12.70	.0142		
47.1	+11.89	.0145		
∞	+9.93			
Average		0.0144		0.105

In 1.4-percent aqueous solution, calcium galacturonate shows a specific rotation of +75.0° (3.9 minutes after dissolution), an equilibrium rotation of +36.8°, and the complex mutarotation reported in table 5. A sample of calcium galacturonate dissolved in a chemically equivalent quantity of dilute nitric acid (table 6) showed an initial rotation of +21.6° *S*, a rapid mutarotation involving a change of 2.3° *S*, and a slow mutarotation involving a change of 9.4° *S*, whereas an aqueous solution of α-*D*-galacturonic acid (table 7) of like concentration showed an initial rotation of +21.6° *S*, a rapid change of 2.1° *S*, and a slow change of 9.5° *S*. The agreement shows that calcium galacturonate contains the alpha pyranose modification and may be designated calcium α-*D*-galacturonate.

(b) PREPARATION FROM CITRUS PECTIN

A mixture consisting of 1 kg of dry citrus pectin (210 grade, containing 84 percent of galacturonic acid by analysis) and 100 g of Pectinol 100D [6] was added with stirring to 10 liters of water. The

[6] A commercial pectinase manufactured by Rohm & Haas, Philadelphia, Pa.

TABLE 7.—*Mutarotation of α-D-galacturonic acid in water saturated with carbon dioxide*

0.002 equivalent of *α-D*-galacturonic acid dissolved in 25 ml of water at 20° C, and read in a 4-dm tube. pH=2.3

$°S=+9.52\times10^{-0.0119t}+2.08\times10^{-0.115t}+10.01$

$[\alpha]_D^{20}=°S\times5.62$ (based on weight of anhydrous galacturonic acid)

Time	Observed reading	m_1	Deviation	m_2
Minutes	°S			
2.2	+20.14		1.16	
4.0	+19.24		0.70	0.122
5.6	+18.66		.48	.113
7.1	+18.18		.33	.111
9.0	+17.64		.19	.116
10.7	+17.24		.13	.112
15.6	+16.22			
20.2	+15.45	0.0125		
26.1	+14.70	.0116		
30.6	+14.14	.0118		
44.1	+12.89	.0117		
∞	+10.01			
Average		0.0119		0.115

aqueous mixture was placed in an oven at 37° C for 2 days. During this period partial hydrolysis of the pectin took place, and the solution became highly acid and less viscous. The acidity was then adjusted to pH 3.9 by the addition of calcium carbonate (about 150 g), and the mixture was kept at 37° C for 5 more days. At this time, reduction values showed that the hydrolysis was substantially complete. The solution was heated to 80° C, neutralized with calcium carbonate, filtered, and concentrated in a vacuum still at about 40° C to a volume of 2 liters. During the evaporation considerable calcium galacturonate crystallized. The crystalline mixture was diluted with 500 ml of ethyl alcohol and allowed to stand over-night at 37° C. The crystals were separated by filtration, washed with aqueous alcohol, and recrystallized from 10 parts of hot water. The yield of pure calcium galacturonate (700 g) was 73 percent of the theoretical. Satisfactory results, but with somewhat lower yields, were obtained without the use of alcohol.

(c) CONVERSION TO GALACTURONIC ACID

A mixture consisting of 444 g of calcium galacturonate (1 mole) and 126 g of oxalic acid (1 mole) was added with stirring to 2 liters of hot water. The resulting calcium oxalate was separated by filtration and washed with hot water. The filtrate was concentrated to a sirup in a vacuum still at a temperature of 30° C. The sirup was seeded with *α-D*-galacturonic acid monohydrate, and evaporation was continued until the crystalline mixture in the distillation flask became thick. The crystals were separated by filtration and dried at room temperature. The first crop weighed 375 g, and additional crystalline galacturonic acid obtained by concentrating the mother liquor made the yield nearly quantitative.[7] Under the conditions described, little or no decomposition takes place, but if during the evaporation the temperature is allowed to rise, the solution darkens, and the yield is less. Although crystallization from aqueous solution is convenient for large

[7] Satisfactory results were obtained also by the use of sulfuric acid in place of oxalic acid. When sulfuric acid is used, an excess must be carefully avoided.

quantities, crystallization from aqueous alcohol, or aqueous acetic acid, is preferable for small quantities, because there is less loss in handling the material.

7. STRONTIUM GALACTURONATE, $Sr(C_6H_9O_7)_2.5H_2O$

Crystals of strontium galacturonate were first obtained by the addition of a small amount of water to a finely powdered mixture of equivalent quantities of *α-D*-galacturonic acid and strontium carbonate. The seed crystals thus obtained were used in subsequent preparations. The salt was prepared in quantity by neutralizing a 10-percent solution of galacturonic acid in hot water with a strontium carbonate, filtering, and adding ethyl alcohol to saturation. The solution was allowed to cool slowly, since the crystals so obtained are larger and have better filtering properties than those formed from concentrated aqueous solution or by the addition of alcohol to a solution at room temperature. The compound was recrystallized from aqueous alcohol, separated, and dried in a vacuum desiccator at room temperature over calcium chloride. At 20° C a saturated aqueous solution of strontium galacturonate pentahydrate contains 3.0 g per 100 ml of solution.

Analysis: Calculated for $SrC_{12}H_{28}O_{19}$: C, 25.6; H, 5.0. Found: C, 25.8; H, 5.0.

In 1.4-percent aqueous solution, strontium galacturonate shows a specific rotation of +63.1° (2.7 minutes after dissolution), an equilibrium rotation of +29.1°, and a complex mutarotation. A sample containing 0.002 equivalent of strontium galacturonate, when dissolved in 25 ml of 0.08 *N* nitric acid, showed an initial rotation of +21.7° *S*, a rapid mutarotation involving a change of 2.4° *S*, and a slow mutarotation involving a change of 9.3° *S* (equation given in table 1). These values are in substantial agreement with the values obtained from similar measurements with *α-D*-galacturonic acid. Hence the new salt may be designated strontium *α-D*-galacturonate.

8. SODIUM CALCIUM GALACTURONATE, $NaCa(C_6H_9O_7)_3.6H_2O$

(a) PREPARATION FROM GALACTURONIC ACID

This new crystalline salt (see footnote 3, page 78) was prepared by treating a solution containing 3 equivalents of galacturonic acid with 1 equivalent of sodium hydroxide and an excess of calcium carbonate. The mixture was filtered and concentrated under reduced pressure until crystallization took place. For analysis the salt was recrystallized from hot water, and dried in a vacuum desiccator at room temperature over calcium chloride. The yield of the double salt was substantially quantitative.

The salt crystallizes readily from hot water, in which it is soluble to the extent of approximately 15 g per 100 ml. At 20° C the solubility in water is only 1.8 g per 100 ml of solution. The facility with which it crystallizes, its low solubility, and other desirable properties make the compound of unusual importance for the separation of galacturonic acid.

Analysis: Calculated for $NaCaC_{18}H_{39}O_{27}$: Ca, 5.3; C, 28.8; H, 5.2. Found: Ca, 5.4; C, 28.8; H, 5.2.

The salt might be composed of alpha galacturonate radicals, of beta galacturonate radicals, or of alpha and beta galacturonate radicals in

the proportions of 1:2 or 2:1. In 1.4-percent aqueous solution it shows a specific rotation of +61.7° (3.4 minutes after dissolution), an equilibrium rotation of +32.4°, and a complex mutarotation. A sample of sodium calcium galacturonate containing 0.002 equivalent when dissolved in 25 ml of 0.08 normal nitric acid showed an initial rotation of +21.9°*S*, a rapid mutarotation involving a change of 2.5°*S*, and a slow change of 9.3°*S*, whereas a sample of *α-D*-galacturonic acid of like concentration showed an initial rotation of +21.7°*S*, a rapid mutarotation involving a change of 2.1°*S*, and a slow change of 9.5°*S* (equation given in table 1). The agreement of the mutarotation of the acidified salt with that of *α-D*-galacturonic acid shows that the crystalline salt contains only the alpha pyranose modification of the acid.

(b) PREPARATION FROM PECTIC ACID[8]

Sodium calcium galacturonate is particularly useful for separating galacturonic acid from the hydrolytic liquors of plant materials. The process described here involves enzymatic hydrolysis of a mixture of pectic acid and sodium pectate, followed by neutralization of the hydrolyzate with calcium carbonate and crystallization of the resulting sodium calcium galacturonate. The procedure, which is described in considerable detail, is suitable for the production of either large or small quantities of the salt.

Dry pectic acid and sodium bicarbonate were mixed in such proportion[9] that the acidity of the mixture in 7 parts of water was between pH 3.8 and 4.0. One kilogram of dry sodium bicarbonate,pectic acid mixture was added in portions with stirring to 7 liters of water. The carbon dioxide liberated caused considerable foaming, which was kept under control by the addition of an antifoam agent (hexyl alcohol). Fifty grams of Pectinol 100D (see footnote 6, page 87) and sufficient toluene to prevent mold growth were added, and the mixture was allowed to stand at 37° C until hydrolysis was complete, (about 8 days). The material was then heated to about 80° C and neutralized with calcium carbonate. About 50 g of calcium carbonate was required. After the addition of 150 g of calcium nitrate,[10] $Ca(NO_3)_2 \cdot 4H_2O$, the mixture was heated to boiling and filtered with the aid of 25 g of decolorizing carbon and 25 g of infusorial earth. The residue on the filter was washed with 3 liters of hot water containing 25 g of calcium nitrate.

The filtered solution was evaporated[11] under reduced pressure at a temperature below 50° C. Crystallization of sodium calcium galacturonate took place as evaporation proceeded; the process was interrupted and the crystals were separated when the mixture of crystals and sirup reached a convenient consistency. Additional material was obtained by evaporation of the mother liquor. The yield of relatively pure crystalline sodium calcium galacturonate was approximately 750 g, or 85 percent of the galacturonic acid content of the

[8] The product was supplied by the California Fruit Growers' Exchange, Ontario, Calif.

[9] Usually about 1 part of sodium bicarbonate is required for 4 to 5 parts of pectic acid, but the amount varies for different lots. The proportion for each batch of pectic acid may be ascertained by mixing 5-g samples with various amounts of sodium bicarbonate and determining the pH of the mixture in 35 ml of water. When this proportion has been ascertained for the particular pectic acid employed, the trial adjustment is unnecessary in subsequent preparations, but the pH of the mixture to be hydrolyzed should always be checked.

[10] The addition of calcium nitrate at this point causes coagulation of the colloidal material and greatly facilitates filtration. Calcium nitrate is necessary in the wash water to prevent peptization of the residue. The total amount of calcium ion added must be sufficient for the formation of the double salt.

[11] A substantial crop of crystalline sodium calcium galacturonate may be obtained without evaporation if the liquid is cooled, seeded, and allowed to stand.

pectic acid used. Analyses of three samples of commercial pectic acid by the carbon dioxide method showed the presence of galacturonic acid corresponding to 85, 90, and 95 percent of the pectic acid. In the example reported above, the pectic acid having the lowest galacturonic acid content was used. Higher yields were obtained with the other samples.

(c) CONVERSION TO SODIUM GALACTURONATE

A mixture consisting of 0.5 mole (375.3 g) of dry sodium calcium galacturonate and 0.5 mole (67 g) of sodium oxalate was added in small portions with stirring to 2 liters of hot water. The resulting calcium oxalate was separated by filtration. The filtrate was concentrated under reduced pressure at 45° C to a thin sirup, which was saturated with ethyl alcohol and seeded with crystalline sodium galacturonate. When crystallization was substantially complete, the crystals were separated by filtration and washed with aqueous alcohol. The first crop weighed 310 g. Additional crystals obtained by concentrating the mother liquor made the yield substantially quantitative.

(d) CONVERSION TO GALACTURONIC ACID

One mole (750.6 g) of sodium calcium galacturonate was mixed with exactly 1,500 ml of 2 *N* aqueous sulfuric acid, and the resulting calcium sulfate was separated by filtration. The solution was concentrated at 30° C under reduced pressure to a volume of about 800 ml, and 200 ml of 50-percent aqueous acetic acid and seed crystals of galacturonic acid hydrate were added. Crystallization was allowed to take place under constant stirring at room temperature. The crystals were collected on a filter and washed with aqueous acetic acid. The first crop (440 g) $[\alpha]_D^{20}=+51.8°$, was relatively pure galacturonic acid hydrate. By concentrating the mother liquor, additional crops of 60 g, $[\alpha]_D^{20}=+48.0°$, and 20 g, $[\alpha]_D=+48.5°$, were obtained. The total, 520 g, corresponds to 82 percent of the theoretical yield.

9. SODIUM STRONTIUM GALACTURONATE, $NaSr(C_6H_9O_7)_3.6H_2O$

This salt was prepared by neutralizing a solution containing 2 equivalents of *α-D*-galacturonic acid with strontium carbonate, and combining this with a solution containing 1 equivalent of sodium galacturonate. The salt separates readily and can be recrystallized from about 7 parts of hot water. At 20° C it is soluble only to the extent of 1.6 g per 100 ml. For analysis the recrystallized salt was dried over calcium chloride at room temperature in a vacuum desiccator.

Analysis: Calculated for $NaSrC_{18}H_{39}O_{27}$: Sr, 11.0; C, 27.1; H, 4.9. Found: Sr, 11.0; C, 26.9; H, 4.8.

In 1.4-percent aqueous solution, sodium strontium galacturonate shows a specific rotation of +48.3° (4.0 minutes after dissolution), an equilibrium rotation of +30.2°, and a complex mutarotation. The mutarotation which takes place when the compound is dissolved in an equivalent quantity of dilute nitric acid (table 1) follows substantially the same equation as the mutarotation of *α-D*-galacturonic acid in water. The initial rotation and the course of the mutarotation show that the crystalline compound contains the alpha pyranose modification of galacturonic acid.

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10. SODIUM BARIUM GALACTURONATE, $NaBa(C_6H_9O_7)_3.6H_2O$

A mixture consisting of 25 g of sodium calcium galacturonate and 4.2 g of powdered oxalic acid was added in portions to 40 ml of hot water. After several minutes, 7 g of barium carbonate was added and when reaction was complete the mixture was filtered. The filtered solution was placed in the refrigerator. In the course of 1 day, crystalline sodium barium galacturonate separated in good yield. The product was recrystallized from a minimum amount of hot water and for analysis dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $NaBaC_{18}H_{39}O_{27}$: C, 25.5; H, 4.6. Found: C, 25.5; H, 4.8.

In 1.4-percent aqueous solution, sodium barium galacturonate shows a specific rotation of +57.2° (3.9 minutes after dissolution), an equilibrium rotation of +27.8°, and a complex mutarotation. The mutarotation which takes place when the compound is dissolved in an equivalent quantity of dilute nitric acid (table 1) shows that the crystalline substance contains the alpha pyranose modification of galacturonic acid.

11. SODIUM CADMIUM GALACTURONATE, $NaCd(C_6H_9O_7)_3.6H_2O$

This salt was prepared by neutralizing a solution containing 2 equivalents of *D*-galacturonic acid with cadmium hydroxide, and combining this with a solution containing 1 equivalent of sodium galacturonate. The solution was filtered and evaporated to a thin sirup, from which the crystalline salt separated in the course of a day. The salt was recrystallized by dissolving it in a small quantity of water, and adding ethyl alcohol to the point of saturation. The crystals that separated were collected on a filter, washed with aqueous alcohol, and dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $NaCdC_{18}H_{39}O_{27}$: C, 26.3; H, 4.8. Found: C, 26.6; H, 4.9.

In 1.4-percent aqueous solution, sodium cadmium galacturonate shows a specific rotation of +53.3° (2.1 minutes after dissolution), an equilibrium rotation of +27.3°, and a complex mutarotation. The mutarotation which takes place when the compound is dissolved in an equivalent quantity of dilute nitric acid shows that the crystalline substance contains the alpha pyranose modification of galacturonic acid. The mutarotation data for the substance in an equivalent quantity of nitric acid is given in the form of an equation in table 1.

12. SODIUM LEAD GALACTURONATE, $NaPb(C_6H_9O_7)_3.6H_2O$

A mixture of 30 g finely powdered sodium calcium galacturonate and 5.5 g of oxalic acid was added to 45 ml of water. The mixture was stirred for 15 minutes, after which an excess of freshly prepared normal lead carbonate was added, and stirring was continued for 15 minutes. Then the mixture was filtered with the aid of decolorizing carbon, and the filtrate was allowed to stand in the refrigerator overnight. The crystalline sodium lead galacturonate which formed was

separated by filtration and washed with aqueous ethyl alcohol (7 parts of water to 1 part of alcohol). The product was recrystallized from water and dried in a vacuum desiccator over calcium chloride at room temperature. Sodium lead galacturonate crystallizes from fairly concentrated aqueous solutions; it is necessary to avoid overheating, since decomposition of the salt in solution takes place readily.

Analysis: Calculated for $NaPbC_{18}H_{39}O_{27}$: C, 23.6; H, 4.3. Found: C, 23.6; H, 4.2

In 1.4-percent aqueous solution, sodium lead galacturonate gives an equilibrium specific rotation of +29.0°. Presumably because of the catalytic action of the lead ion the mutarotation is too rapid to be measured. In the presence of dilute nitric acid, the mutarotation reaction (table 1) is more rapid than that of the other double salts reported here, but it is undoubtedly of like character. Hence it is concluded that the crystalline sodium lead salt contains the alpha pyranose modification of galacturonic acid.

13. POTASSIUM CALCIUM GALACTURONATE, $KCa(C_6H_9O_7)_3.6H_2O$

Ten grams of galacturonic acid monohydrate was mixed with 1.09 g of potassium carbonate in 50 ml of water. Calcium carbonate was then added, and after a few minutes the excess was removed by filtration. The solution was saturated with ethyl alcohol and brought to crystallization by scratching the walls of the container with a glass rod. The crystalline material was separated and recrystallized by dissolving in water at room temperature, and adding alcohol. If alcohol is added to a warm, aqueous solution, normal calcium galacturonate will crystallize in place of the double salt. For analysis the recrystallized potassium calcium galacturonate was dried in a vacuum desiccator at room temperature over calcium chloride.

Analysis: Calculated for $KCaC_{18}H_{39}O_{27}$: Ca, 5.2; C, 28.2; H, 5.1. Found: Ca, 5.3; C, 28.2; H, 5.1.

In 1.4-percent aqueous solution the salt shows a specific rotation of +69.2° (1.6 minutes after dissolution), an equilibrium rotation of +31.4°, and a complex mutarotation. The mutarotation which takes place when the salt is dissolved in an equivalent quantity of dilute nitric acid is similar to that of α-*D*-galacturonic acid in water and follows nearly the same equation (table 1). Hence the double salt is a derivative of the alpha pyranose modification of crystalline galacturonic acid.

IV. SUMMARY

The salts listed in table 8 have been prepared and their properties studied. With the exception of the sodium salt, all the compounds are new crystalline substances. The sodium salt reported here contains the beta pyranose modification and appears to differ from that previously reported in that it exhibits mutarotation. A unique class of double salts containing a monovalent and a divalent metal in combination with three alpha galacturonate radicals was discovered, and the use of sodium calcium galacturonate and of calcium galacturonate for the preparation of galacturonic acid from pectic substances was described.

TABLE 8.—*Salts of galacturonic acid*

Salt	Optical rotation [a]	C [b]	Modification of acid present
$NaC_6H_9O_7$	+36.0	4	Beta pyranose.
$(KC_6H_9O_7)_2.H_2O$	+31.6	4	Do.
$(NH_4C_6H_9O_7)_2.H_2O$	+35.5	4	Do.
$Cd(C_6H_9O_7)_2.2H_2O$	+28.4	1.4	Do.
$(AgC_6H_9O_7)_2.H_2O$	+25.1	3.2	Do.
$Ca(C_6H_9O_7)_2.H_2O$	+36.8	1.4	Alpha pyranose.
$Sr(C_6H_9O_7)_2.5H_2O$	+29.1	1.4	Do.
$NaCa(C_6H_9O_7)_3.6H_2O$ [c]	+32.4	1.4	Do.
$NaSr(C_6H_9O_7)_3.6H_2O$	+30.2	1.4	Do.
$NaBa(C_6H_9O_7)_3.6H_2O$	+27.8	1.4	Do.
$NaCd(C_6H_9O_7)_3.6H_2O$	+27.3	1.4	Do.
$NaPb(C_6H_9O_7)_3.6H_2O$	+29.0	1.4	Do.
$KCa(C_6H_9O_7)_3.6H_2O$ [c]	+31.4	1.4	Do.

[a] At equilibrium in water.
[b] Concentration of salt in grams per 100 ml of aqueous solution.
[c] See footnote 3, page 78.

The authors express their appreciation to Kenneth Fleischer, who made the carbon and hydrogen analyses reported in the paper.

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NOTE ON THE MACROANALYSIS OF CARBON AND HYDROGEN BY COMBUSTION

By Donald D. Wagman and Frederick D. Rossini

ABSTRACT

This note describes the present state of the development of an analytical combustion apparatus for the accurate determination, on a macro scale, of carbon and hydrogen in hydrocarbons or in compounds containing carbon, hydrogen, and oxygen. The precision and accuracy attainable are indicated by a report of the results of a series of five experiments performed on highly purified benzoic acid.

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I. INTRODUCTION

During the past 15 years, several investigations at the National Bureau of Standards have involved precise analyses of carbon and hydrogen [1, 2, 3, 4, 5, 6].[1] Each of these investigations incorporated in its apparatus such prior improvements as were appropriate and made some new contributions to the problem. This note describes the present state of the development of an analytical combustion apparatus for the accurate determination on a macro scale of carbon and hydrogen in hydrocarbons or in compounds containing carbon, hydrogen, and oxygen. The precision and accuracy attainable with this apparatus are indicated by a report of the results of a series of five experiments performed on highly purified benzoic acid.

II. APPARATUS

The assembly of the apparatus, as used for nonvolatile liquids or solids, is shown in figure 1, in which the letters have the following significance: A, cylinder containing oxygen under pressure; B, reducing valve and flow regulator; C, three-way stopcock, Pyrex glass; D, flow meter, Pyrex glass, containing mercury; E, safety trap, Pyrex glass, containing mercury; L, female connection, Pyrex glass, standard taper; F, combustion tube, quartz, containing copper oxide; G, electric heater; W, graded seal, quartz to Pyrex glass; H, absorption

[1] Figures in brackets indicate the literature references at the end of this paper.

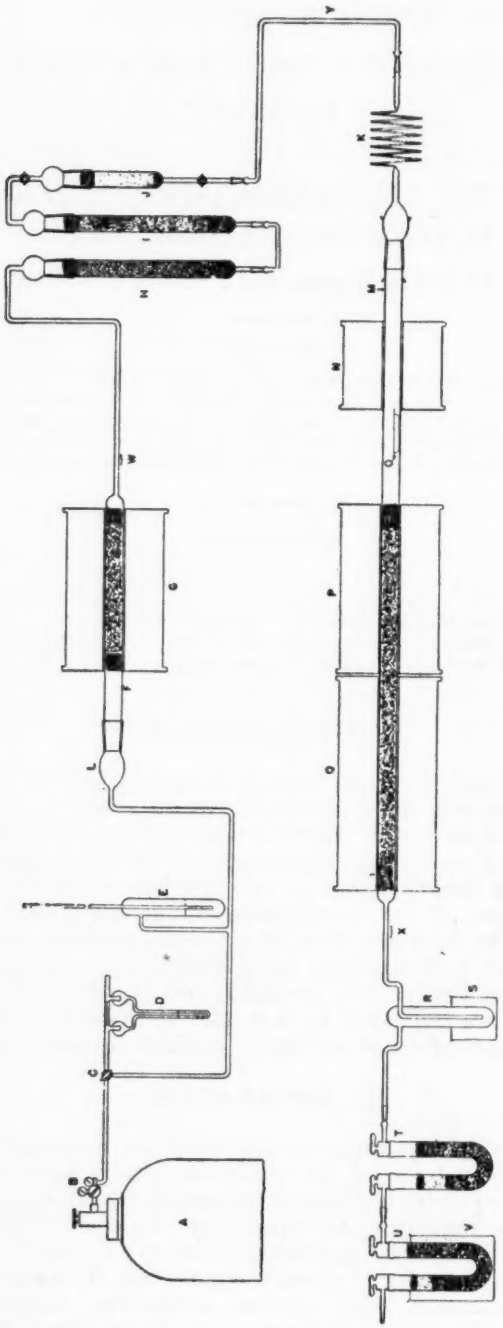

FIGURE 1.—*Assembly of analytical combustion apparatus.*

tube, Pyrex glass, containing Ascarite; I, absorption tube, Pyrex glass, containing magnesium perchlorate; J, absorption tube, Pyrex glass, bounded by stopcocks, Pyrex glass, containing phosphorus pentoxide; Y, connecting tube, Pyrex glass, stationary; K, connecting tube, Pyrex glass, compressible through the coil, having standard tapered ends as indicated; M, combustion tube, quartz, containing the boat (with sample) and copper oxide, as indicated; N, electric heater, for vaporizing sample; O, boat, platinum, containing sample for combustion; P, Q, electric heaters; X, graded seal, quartz to Pyrex glass; R, trap, Pyrex glass, for temporarily condensing excess water; S, beaker, glass, containing water; T, absorption tube, Pyrex glass, containing, in order, magnesium perchlorate and phosphorus pentoxide, each bounded by a layer of dry asbestos; U, absorption tube, Pyrex glass, containing, in order, Ascarite, magnesium perchlorate, and phosphorus pentoxide, each bounded by a layer of dry asbestos; V, beaker, glass, containing water.

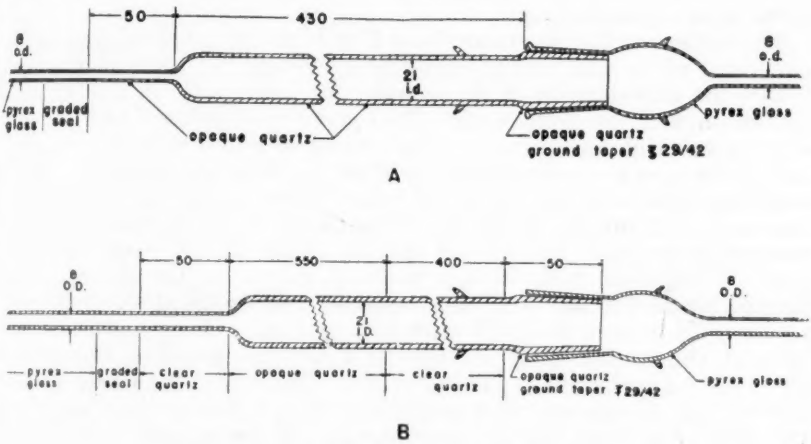

FIGURE 2.—*Details of the combustion tubes.*

A, Combustion tube for purification; *B*, main combustion tube. All dimensions in millimeters.

In figure 2 are shown in detail the combustion tubes F and M, F being the combustion tube for purification of the oxygen and M that for the main reaction of combustion.

III. FILLING, HANDLING, AND WEIGHING THE ABSORPTION TUBES

The manner of filling, handling, and weighing the absorption tubes, and of calculating the true masses of water and carbon dioxide absorbed, is described on pages 6 to 9 and 39 to 41 of reference [2]. With the absorption tubes flushed with water-free and carbon dioxide-free hydrogen just prior to each weighing, and with a duplicate closed absorption tube being used as a counterpoise, the mass of water is

$$m(H_2O)=0.99991(\Delta m), \quad (1)$$

and the mass of carbon dioxide is

$$m(CO_2)=0.99990(\Delta m), \quad (2)$$

where Δm is the apparent increase in mass of the corresponding absorption tube, using brass weights. The numerical factors in eq 1 and 2 include both the buoyant effect of the air on the brass weights and the effect of the change in volume of the solid phase (and consequently of the gas phase) in the absorption tube during the absorption process.

It is important to note the necessity of performing "blank" experiments on each operation which may add to or subtract from the mass of sample, of water, or of carbon dioxide, as described in section V.

The balance and weights, the weighing procedure, and the lubricant employed on the stopcocks and other ground joints, etc., are discussed in the earlier papers to which reference has already been made.

IV. EXPERIMENTAL PROCEDURE FOR COMPOUNDS OF LOW VOLATILITY

The experimental procedure for compounds of low volatility is illustrated by the following operations with benzoic acid as the material under examination:

The entire combustion train, from C to R in figure 1, was thoroughly swept out while cold, using oxygen from cylinder A. About one hour before the introduction of the sample, the heaters G, P, and Q were turned on, and the copper-oxide filled portions of tubes F and M were allowed to reach an operating temperature of about 800° C. During this period, oxygen continued to flow through the system. After combustion tubes F and M had attained their operating temperature, the train was opened at K and a platinum boat, O, containing an accurately weighed amount of sample (near 1.8 g), was placed in tube M approximately at the position shown in the figure. The flexible connecting tube K was replaced and fastened securely into position by means of small wire coil springs. Oxygen was passed through the system for 20 minutes at a rate, measured on flow meter D, of 250 ml per minute. This served to flush out of the whole system any carbon dioxide or water vapor introduced during the short time the train was open for the introduction of the sample. This procedure may be used only for compounds that are sufficiently nonvolatile or very pure, so that no appreciable fractionation of the sample can occur during this flushing period. Following this flushing-out process, the weighed absorption tubes T and U were connected in series with trap R, as shown in figure 1. Tube T contained anhydrous magnesium perchlorate backed with phosphorus pentoxide, each layer of absorbent being bounded with dry asbestos. Tube U contained, in order, Ascarite (commercial mixture of sodium hydroxide and asbestos), anhydrous magnesium perchlorate, and phosphorus pentoxide, each bounded with dry asbestos. To absorb the heat evolved by the reaction of carbon dioxide with the Ascarite, tube U was kept immersed in a beaker of cold distilled water.

With the oxygen still flowing through the system at a rate of 250 ml per minute, heater N was turned on slowly to reach an operating temperature of about 180° C, at which temperature benzoic acid has a vapor pressure of the order of 80 mm Hg. After combustion had begun, as evidenced by the condensation of water in tube R, the exposed parts of combustion tube M, between heaters N and P, were covered with appropriately shaped blocks of magnesia insulation. The combustion then proceeded smoothly to the end, requiring about 2½ hours for the actual combustion.

When the reaction was complete, the flow of oxygen was increased to about 400 ml per minute and allowed to run for 4 hours. If necessary, to facilitate the evaporation of the water condensed in trap R, the cold water in beaker S was replaced with warm water. At the end of this period all of the water and carbon dioxide formed in the combustion was in the absorption tubes T and U, respectively. The oxygen was turned to waste at stopcock C, absorption tubes T and U were closed to each other and to the atmosphere and removed from the train, and the train was capped at the exit end of trap R until the next experiment.

The absorption tubes were handled as mentioned in the preceding section, the lubricant being removed from the end connecting joints with ether. The tubes were then flushed for 10 minutes with water-free and carbon-dioxide-free hydrogen and placed in the balance case. About 30 minutes was allowed for the tubes to come to equilibrium in the balance case before weighing them. The weighing, and reduction of the data to obtain the true masses of water and carbon dioxide absorbed, was performed as described in the preceding section.

"Blank" experiments were performed as follows:

(a) To determine the mass of benzoic acid lost from the sample during the flushing of the train after the sample was introduced but before heater N was turned on.

(b) To determine the increase in weight of the absorption tubes with all operating conditions the same as in a regular combustion experiment except that no benzoic acid was introduced, the train being opened at K as usual, however.

V. EXPERIMENTAL RESULTS ON PURIFIED BENZOIC ACID

The experimental results obtained on purified benzoic acid, using the apparatus and procedure described in the preceding sections, are reported in tables 1 and 2. The benzoic acid used was from a lot of NBS Standard Sample 39f, which had been further purified to serve as a standard for microanalysis. According to the certificate of analysis for NBS Standard Sample 39f, "freezing point measurements indicate a mole percent purity of 99.98" and "on the basis of titration a purity of 100.03 percent is indicated." Since the small amount of impurity will be similar to the parent substance, it is likely to have an insignificant effect on the content of carbon and hydrogen

TABLE 1.—*Results of experiments to determine the change in mass of the absorption tubes, with operating conditions as in a regular combustion experiment, except that no benzoic acid was burned*

Experiment number	Volume of oxygen	Increase in mass of absorption tube for water	Increase in mass of absorption tube for carbon dioxide
	Liters	*g*	*g*
1	120	0.00020	0.00023
2	120	.00070	.00025
3	130	.00035	.00043
Mean	123	0.00042	0.00030
Standard deviation of the mean	-------	±0.00015	±0.00006

in the sample. The actual sample used in the present investigation was found to contain 0.0018 ± 0.0004 percent by weight of water [8].

The results of four experiments to determine the mass of benzoic acid lost in the flushing operation after introduction of the sample, with a flow of oxygen of 250 ml per minute for 15 minutes, gave a mean value of 0.00005 g, with a standard deviation of the mean equal to ± 0.00001 g. Since the flushing operation in the actual experiments involved a flow of oxygen at the rate of 250 ml per minute for 20 minutes, the correction applied in the actual experiments was 20/15 of the mean of the four experiments.

TABLE 2.—*Results on benzoic acid*

Number of experiments	Mean mass of sample [a]	Mean mass of carbon dioxide [b]	Mean mass of water [c]	Carbon in sample [d] (percentage by weight)	Hydrogen in sample [d] (percentage by weight)
5	g 1.84358	g 4.56040	g 0.81628	68.836$_7$	4.954$_6$
Standard deviation of the mean				$\pm 0.001_3$	± 0.0010
Theoretical value [d]				68.843	4.9526
Experimental value minus theoretical value				-0.006 ± 0.003 [e]	$+0.0020 \pm 0.0028$ [e]

[a] Corrected by a "blank" of 0.00006 g and for 0.0018 ± 0.0004 percent by weight of water in the original sample. (See text.)

[b] Corrected by a "blank" of 0.00035 g. (See text and table 1.)

[c] Corrected by a "blank" of 0.00049 g and for 0.0018 ± 0.0004 percent by weight of water in the original sample. (See text and table 1.)

[d] Calculated using the following atomic weights: O, 16.0000; H, 1.0080; C, 12.010.

[e] The uncertainty assigned here is twice the over-all standard deviation [7], including the standard deviations of the "blank" experiments. (See text and tables 1 and 2.)

Table 1 gives the results of three experiments to determine the increase in weight of the absorption tubes when no benzoic acid was burned, all other conditions being the same as in an actual experiment. It was found that the volume of oxygen that flowed through the train was 162, 145, 129, 145, and 136 liters, respectively, in the five experiments, with a mean value of 143 liters. The means of the values in table 1 were therefore multiplied by the factor of 143/123 to give the proper "blank" correction to be applied to the observed increases in mass of the two absorption tubes.

Table 2 gives the mean of the experimental results of a series of five combustion experiments with benzoic acid, with the masses of sample, water absorbed, and carbon dioxide absorbed being obtained by applying the appropriate blank corrections to the respective observed differences in weight, together with a comparison of the experimental results with the theoretical values for benzoic acid.

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THERMAL EXPANSION OF CONCRETE AGGREGATE MATERIALS

By Walter H. Johnson and Willard H. Parsons

ABSTRACT

As a part of a study of the properties of concrete aggregates, thermal-expansion determinations were made on 123 specimens of aggregate materials by the optical interferometer method over the temperature range −20° to +60° C. Additional measurements were made on crystals of calcite, quartz, and feldspar. The thermal expansivities of most aggregate materials are close to or within the range of expansivities of hardened portland cements. Certain exceptions are pointed out. Crystal orientation, rock texture, and composition are discussed with regard to their effects on the relation of the thermal expansion of aggregates to the durability of concrete.

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I. INTRODUCTION

In concrete structures, where resistance to frost action is one of the properties required of the concrete, the thermal expansivity of the aggregate may be an important factor. If, for instance, the thermal expansion of an aggregate differs considerably from that of the cementitious matrix, a potential incompatability exists, which may result in excessive internal stresses if the concrete is subjected to large temperature changes. Pearson [1][1] and also Hornibrook [2]

[1] Figures in brackets indicate the literature references at the end of this paper.

have described concrete failures attributed to an initial weakening of the concrete because of differences between the thermal expansion of the aggregates (which had unusually low coefficients of thermal expansion) and that of the matrix. The weakened concrete then became susceptible to frost action, which caused the actual disruption. This sequence of disintegration has recently been demonstrated in the laboratory by Pearson [3].

Adequate information is lacking on the thermal expansion characteristics of commercial concrete aggregates. Accordingly, as a part of a general study at this Bureau of the properties of aggregate materials, commercial aggregates from a number of sources were obtained and separated into fractions representing the various rocks and minerals constituting the aggregates. Coefficients of linear thermal expansion were then determined for the rocks and minerals over the temperature range of −20° to +60° C (−4° to +140°F). This paper gives a petrographic description of the various rock and mineral fractions of the aggregates, the respective thermal-expansion coefficients of these materials, and a discussion of the factors which may effect the thermal expansion in relation to concrete.

Some problems encountered during the present investigation warrant further study, and additional thermal-expansion measurements should be made on certain of the aggregate materials herein considered. Due to the pressure of the wartime emergency, however, these studies cannot be continued at this time.

II. PREVIOUS WORK

Griffith [4] has made thermal-expansion measurements on a considerable number of rocks from room temperature to 500° F; he also made some measurements between 32° F and room temperature. Willis and De Reus [5] measured the thermal expansion of wet and dry specimens of chert, quartzite, sandstone, basalt, granite, limestone, and dolomite between 37° and 140° F. Koenitzer [6] measured the expansion of marble and calcite between −25° and +212° F. Souder and Hidnert [7] have made thermal-expansion measurements on marble and have shown that permanent changes occur with succeeding temperature cycles. (A comparison of some of these results with those of the present investigation will be given later.) Davis [8] and others [5, 6, and 9] have measured the thermal expansion of hardened portland cements, mortars, and concretes under various conditions. They have shown the effects of such factors as water saturation, extreme drying, steaming, richness of mix, and age on the thermal expansion.

An examination of the available data shows that there is very little information regarding the thermal dilation of the aggregate materials within the temperature range of natural weather conditions. The majority of investigators, furthermore, have assumed a more or less straight-line relationship between temperature and thermal expansion, without regard to possible irregularities during the large intervals between readings. Although the expansion of various materials, when plotted against temperature, usually yield smooth curves, it will be shown that there are some glaring exceptions. In this investigation, therefore, the length changes of the aggregate materials have been followed continuously from −25° to +65° C and from +65° to −5° C.

III. TEST METHOD

1. APPARATUS AND CALIBRATION

(a) GENERAL DESCRIPTION

The interferometer method described by Merritt [10] and modified by Saunders [11] was used in conjunction with a thermal chamber that could be varied continuously between −25° and +65° C. This permitted the use of small specimens, the measurement of low expansivities, and the taking of frequent observations separated by small temperature intervals. The thermal chamber (fig. 1) consisted essentially of a closed brass cylinder, about 9 in. high and 3 in. in diameter, inserted through the top of a remodeled household refrigerator into a tank of kerosine which surrounded the freezing coils. A hard-rubber tube wound with 30 ft. of No. 24 Nichrome resistance wire served as

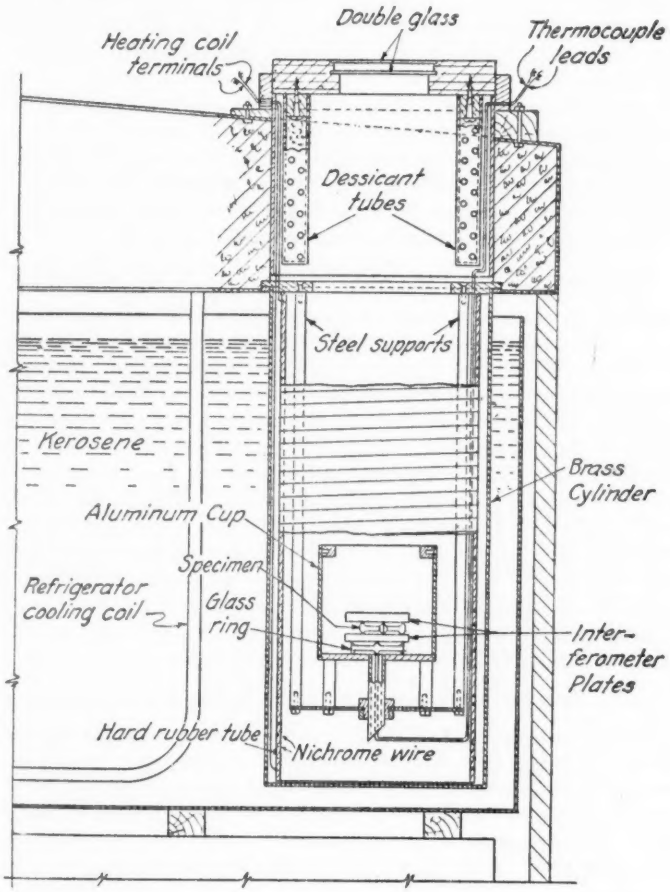

FIGURE 1.—*Schematic diagram of thermal chamber.*

the heating element. The specimen and interferometer plates were supported from the top of the cylinder by ¼-in. steel rods. The top was closed by means of a plastic lid fitted with a double glass window. Perforated brass tubes were filled with absorbent cotton, which served as a desiccant. These tubes were removable and were dried at 105° to 110° C before each test. The lower interferometer plate was separated from the bottom of the aluminum specimen cup by means of a glass ring cut from a piece of tubing and ground in such a way that there were three equidistant bearing surfaces on the top and three on the bottom.

About half of the expansion measurements were made by the visual method. The temperatures were measured by means of a three-junction copper-constantan thermocouple [12], the variable junctions of which were situated just beneath the lower interferometer plate. The emf of the thermocouple was measured by means of a portable potentiometer. Later, a recording camera was constructed, which was a simplified form of one designed by J. B. Saunders of this Bureau. This method consisted essentially in replacing the eyepiece of the interferometer with a narrow slit through which a portion of the interference pattern was photographed on a strip of moving film. By means of a refraction thermometer [13] used in place of the lower interferometer plate, the temperature was recorded simultaneously with the expansion. This method not only eliminates the tedious counting of interference fringes but gives a permanent record of the behavior, which may be checked and rechecked at will.

(b) ESTABLISHMENT OF HEATING AND COOLING SCHEDULE

An arbitrary heating and cooling rate of ½° C per minute was adopted. This permitted a complete temperature cycle in 6 hours, a period sufficiently within the limits of the working day to permit such preliminary adjustments and maintenance as was ordinarily required. By leaving the refrigerating unit in operation overnight, the start could be made at the minimum temperature. The compressor was then stopped and the heating current increased at 15-minute intervals in increments varying from 0.1 to 0.2 ampere. When the desired temperature of 65° C was reached, the refrigerator was again started and the heating current decreased at regular intervals until the temperature had fallen below 0° C. It was found, after some preliminary trials, that below 0° C further cooling was so slow that a uniform cooling rate could no longer be maintained. For this reason, measurements on cooling were not usually taken below −5° C.

(c) CALIBRATION OF THERMOCOUPLE AND REFRACTION THERMOMETER

The thermocouple, which was prepared from previously calibrated wire, was compared with a carefully calibrated mercury-in-glass thermometer and was found to be accurate within ±0.1° C. The variable junctions of the thermocouple were attached directly to the refraction thermometer, and the assembly was then transferred to the thermal chamber. The mean emf value corresponding to each interference fringe was determined by heating and cooling through several temperature cycles, according to schedule, and recording the emf for the passage of each fringe across the reference mark of the thermometer. The accuracy of the temperatures, as measured by this refraction thermometer, was found to be within ±0.2° C.

(d) DETERMINATION OF TEMPERATURE LAG IN TEST SPECIMEN

The actual temperature of the specimen, for a given thermocouple reading, was determined by means of a small quartz refraction thermometer placed between the interferometer plates and separated from them by small grains of sand. The temperature reading of the thermometer was found to lag several degrees behind that of the thermocouple when heating or cooling. As this thermometer had about the same mass as that of the specimens to be measured, the assumption was made that the temperature lag would be about the same in each case. Several temperature cycles were made according to the current-time schedule previously adopted, and emf-temperature curves were drawn from the data obtained. These curves were used to determine the temperatures under actual operating conditions. When measurements were made with the recording apparatus the temperature of the specimen was assumed to be the same as that of the refraction thermometer.

2. PREPARATION OF SPECIMENS

The majority of the specimens were taken from gravel ranging from ¾ in to 1½ in. in diameter. A few were taken from larger pieces of stone, and in some cases specimens were cut from material less than ½ in. in diameter. Figure 2 (a, b, c, d, e, and f) shows, schematically, the successive steps in the preparation of a test specimen. Slabs (a), ranging in thickness from 0.2 in. to 0.4 in., were cut from each specimen, and triangular pieces (b), having sides of about ¾ in., were cut

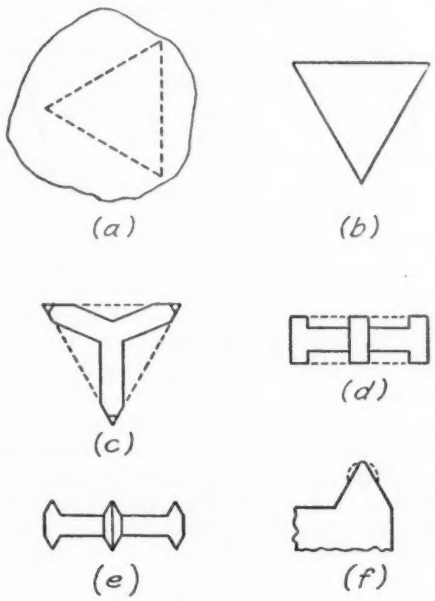

FIGURE 2.—*Schematic diagrams to show successive steps in the preparation of a test specimen.*

(a) Original flat slab marked for further cutting; (b) triangular slab; (c) arms cut from triangular slab leaving a Y-shaped specimen; (d) side view of (c) after grinding it to form the spacers; (e) points cut on spacers; (f) enlarged part of one spacer, showing rounding of its point.

from the slabs. The sides of the triangular-shaped pieces were prepared by grinding on a small silicon carbide wheel to leave a Y-shaped specimen (c) having one arm slightly longer than the others. Portions of the top and bottom of each arm were then ground to form two small projections (d), these two projections forming a spacer. The spacers were pointed as shown (e), care being taken that the top point of each spacer was vertically above lower contact point. By means of a micrometer gage and an emery stone, the heights of the spacers were equalized to within 0.001 in. The projections were slightly rounded (f) by rubbing on a very fine emery stone. The spacers of the finished specimens were about 0.25 in. in height.

The nearly completed specimen was placed between interferometer plates and examined through a viewing instrument. The interference pattern observed usually consisted of very narrow fringes, and a slight pressure on the upper plate caused these fringes to move toward the tallest spacer of the specimen [10]. The heights of the spacers were adjusted by grinding them carefully until the fringes were of the desired width and the tallest spacer was on the longest arm [11]. The tips of the spacers were usually polished sufficiently in the process to show the points of contact with the upper interferometer plate as tiny spots surrounded by Newton rings, and the point on the longest arm was used as a reference point for counting the fringes. When this point could not be seen, a small grain of sand or a piece of fine wire was placed directly over the estimated point of contact for reference. The finished specimen was placed in a desiccator containing calcium chloride for several days before testing.

3. TEST PROCEDURE

The specimen was placed on the lower quartz plate and the upper plate placed so that the reference spacer of the specimen was as near as possible to the center of the plate. When this did not permit sufficient overweighting, a small weight was placed on the upper plate near the point of contact of the reference spacer with the plate [11]. The cup, with plates and specimen as described above, was lowered into the thermal chamber, and the lid and viewing instrument were placed in position. The temperature was then raised to about 65° C to remove as nearly as possible any air film between the points of contact of the specimen with the interferometer plates, after which the thermal chamber was allowed to cool overnight with the refrigerator in operation. On the following morning, the emf and fringe readings were recorded and the heating and cooling cycles carried through as previously described.

The measurements were repeated for those materials which displayed abnormal expansivities or whenever an error in the data was suspected. Several specimens, measured by the visual method, were remeasured by means of the recording apparatus; the results obtained for the two methods were found to agree within the limits of experimental error (on the order of $\pm 0.1 \times 10^{-6}$ per degree centigrade).

4. RELIABILITY OF RESULTS

In order to test the performance of the apparatus and the accuracy of the calibrations, samples of known thermal expansion were obtained from the Thermal Expansion Section of this Bureau and were tested in the manner described. A comparison of the results obtained is as follows:

Sample	Temperature interval	Coefficient of linear thermal expansion per degree centigrade	
		Hidnert [a]	Johnson
	°C		
P	20 to 60	29.0×10^{-6}	29.1×10^{-6}
Q	−20 to 0	11.0×10^{-6}	11.0×10^{-6}
Q	0 to 20	11.3×10^{-6}	11.3×10^{-6}
Q	20 to 60	12.1×10^{-6}	12.1×10^{-6}
R	20 to 60	0.38×10^{-6}	0.4×10^{-6}

[a] Peter Hidnert, Thermal Expansion Section, National Bureau of Standards

IV. DESCRIPTION OF MATERIALS TESTED

Commercial aggregates from 26 different sources were divided into various rock and mineral fractions (table 1). Specimens of these rocks and minerals and of some related materials, whose thermal expansion behaviors are reported in the present study, were examined with a petrographic microscope. The results of these examinations, together with designations of source, classification, and texture, are shown in table 2. The mineral compositions were determined by microscopic study of thin sections and the relative amounts or percentages of each mineral were estimated without a quantitative microscopic count. The percentage values given in table 2 are, therefore, approximations. The naming, or classification, of the rocks has followed common geologic and petrographic usage.

Under the heading of texture (table 2), noncrystalline materials are described as amorphous or glassy; specimens cut from single crystals are so indicated; and the grain size is given for minerals or rocks composed of many particles or crystals. The grain-size terminology refers to actual sizes in millimeters as follows:

Very fine-grained	Less than 0.02.
Fine-grained	0.02 to 0.2.
Medium-grained	0.2 to 2.0.
Coarse-grained	2.0 to 10.0.
Very coarse-grained	Over 10.0.

For rocks of porphyritic texture (most of the rocks between specimens 75 and 94), the grain size in the groundmass is given first and is followed by the grain size of the larger crystals, or so-called phenocrysts. Similarly, with breccias (some of the rocks between specimens 95 and 104), the grain sizes of both the groundmass and of the larger fragments are given.

TABLE 1.—*Approximate percentages of rock and mineral fractions in various commercial concrete aggregates*

Designations	Source of aggregate	Percentage of rock and mineral fractions																		
		Chert	Quartz pebbles	Unclassified sandstones	Limonitic and hematitic sandstones	Clayey, chloritic, and micaceous sandstones	Arkosic and feldspathic sandstones	Limestone	Dolomite	Quartzites [a]	Granite	Other granitic rocks [b]	Felsites: dacite, andesite, trachyte	Basalt	Volcanic breccia	Argillite	Phyllite	Schists and gneisses	Greenstone	Miscellaneous rock types
A	Buck Dam, Va.																100			
B	Potomac River, Md.-Va.	11	30		8	7				[b]39	2							3		
C	Silver Hill, Md.	17	50	15	1					17										
D	Pt. Jefferson, N. Y.		80							7	5							8		
E	Lyon Mt., N. Y.											60		35						5
F	Norwood, N. Y.								100											
G	Jordanville, N. Y.							100												
H	N. LeRoy, N. Y.	[c]20						80												
I	Mille Roche, Canada							100												
J	North Central Ohio	[c]95						5												
K	Camden, Tenn.	100																		
L	Cumberland River, Tenn.	100																		
M	Estill Springs, Tenn.	100																		
N-1	Kentucky Dam area, Tenn, bank gravel	99		1																
N-2	Kentucky Dam area, Tenn, river gravel	99		1																
O	Tishomingo, Miss.	100																		
P	Winn Parish, La.							100												
Q	Elgin, Ill.	4							[e]92									4		
R	Bethany Falls, Mo.							100												
S	St. Louis Co., Mo.							100												
T	Reading, Mo.	95								5										
U	Kimball, Nebr.							[g]4			[i]90		2					4		
V	Bill Williams, Ariz.		7				2			2	41		10	17				19		2
W	Paso Robles, Calif.							[f]100												
X	Kutras, Calif.	[d]6				25	17					8	7	4	5			4	18	[h]6
Y	Cowlitz River, Wash.						13					3	59		21				4	
Z	Spokane, Wash.									[j]49		19				32				

[a] Includes ferruginous, chloritic, feldspathic, micaceous, and calcareous quartzites.
[b] Includes syenite (Lyon Mt.), monzonite, granodiorite, diorite, and gabbro.
[c] Calcareous chert.
[d] Micaceous chert.
[e] Includes 8% of sandy limonitic dolomite.
[f] Includes 18% of pure siliceous quartzites.
[g] Includes some siliceous limestone.
[i] Occurs as gravel, about half of the pebbles are separate quartz or feldspar fragments.
[h] Includes 5% of serpentine.

[c] Calcareous chert.
[d] Micaceous chert.
[e] Soft, sandy limestone.
[f] Quartz (chloritic) limestone.
[g] Includes 18% of pure siliceous quartzites.
[h] Includes some siliceous limestone.
[i] Occurs as gravel; about half of the pebbles are separate quartz or feldspar fragments.
[j] Includes 5% of serpentine.

TABLE 2.—*Description, source, thermal-expansion coefficients, texture, and mineral composition of all materials tested*

Specimen number	Description	Source	Designation in table 1	Mean coefficient of linear thermal expansion per degree C x 10^6			Texture [a]	Mineral constituents [b] (in decreasing order of abundance; percentages approximate only)	
				−20° to +60°	0° to +60°	+60° to 0°		Major, more than 3 percent	Minor, less than 3 percent
1	Quartz (measured perpendicular to c-axis).	Minas Geraes, Brazil	------	13.5	14.0	13.5	Single crystal	Quartz	
2	Quartz (measured parallel to c-axis).	do	------	7.4	7.7	7.7	do	Same crystal as specimen 1	
3	Quartz, pale yellow	Potomac River gravel, Md.-Va.	B	12.9	13.1	13.5	Coarse and fine	Quartz	Trace of limonite.
4	do	do	B	12.7	12.8	13.5	do	do	Do.
5	Quartz, milky	Port Jefferson gravel, Long Island, N. Y.	D	13.5	13.8	13.8	Coarse	do	
6	Quartz, pale yellow	do	D	11.8	11.8	12.0	do	do	Do.
7	Quartz, colorless	do	D	11.7	12.8	12.4	do	do	
8	Quartzite, light-colored	Potomac River gravel, Md.-Va.	B	11.3	12.0	12.9	Medium	Quartz 99%	Traces of kaolin, limonite.
9	Quartzite, brown	do	B	10.3	10.4	10.9	do	do	Limonite; trace of kaolin.
10	Quartzite, tan-gray	do	B	11.9	12.1	12.7	do	Quartz 95%, goethite 4%	Limonite.
11	Quartzite, greenish-gray	do	B	10.7	11.1	11.1	Fine	Quartz 94%, chlorite 5%	Chalc.; trace mica, limo.
12	Quartzite, feldspathic	Port Jefferson gravel, Long Island, N. Y.	D	7.0	7.5	7.5	Medium	Quartz 90%, feldspar, biotite	
13	do	do	D	12.2	12.5	12.8	do	Quartz, feldspar, biotite	
14	Quartzite, light-colored	Spokane gravel, Irvin, Wash	Z	7.6	7.9	8.4	Fine	Quartz 93%, sericite 3%	Musc. 2%, calcite 2%, plagioclase.
15	Quartzite, micaceous	do	Z	9.0	8.7	9.8	do	Quartz 65%, sericite 25%, biotite 10%.	Trace of titanite, leucoxene.
16	Quartzite, calcareous micaceous.	do	Z	9.5	9.3	9.8	do	Quartz 55%, cal. 25%, groundmass of microq. and sericite 20%.	Musc. 2%, pc.; traces of titanite and leucoxene.
17	Sandstone, hematitic	Potomac River gravel, Md.-Va.	B	7.5	1.5	9.4	do	Quartz 94%, hematite 3%	Mica 3%; traces pc., limo., py.
18	Sandstone, limonitic	do	B	9.4	8.7	10.4	do	Quartz 94%, limo. and goethite 5%.	Chalc.; traces of mica, feldspar titanite.
19	do	do	B	8.5	7.0	10.2	do	Quartz 96%, limo. and goethite 3%.	Chalc.; traces of mica, feldspar, zircon.
20	do	do	B	10.1	9.5	10.9	do	Quartz 92%, limo. and goethite (clayey and carb.) 8%.	Mica; traces chalc., feldspar, titanite, zircon.
21	Sandstone, chloritic	do	B	10.4	10.3	11.0	do	Quartz 80%, sericite 10%, chlorite 6%.	Limo. 2%, musc. 2%, bio.; traces of chalc., feldspar, titanite.

See footnotes at end of table.

TABLE 2.—*Description, source, thermal-expansion coefficients, texture, and mineral composition of all materials tested*—Continued.

Specimen number	Description	Source	Designation in table 1	Mean coefficient of linear thermal expansion per degree C x 10^6			Texture [a]	Mineral constituents [b] (in decreasing order of abundance; percentages approximate only)	
				−20° to +60°	0° to +60°	+60° to 0°		Major, more than 3 percent	Minor, less than 3 percent
22	Sandstone, calcareous feldspathic.	Bill Williams gravel (Parker Dam), Ariz.	V	5.1	5.0	5.7	Medium	Feldspar and quartz cemented by cal.; sericite, hema.	Microcline, limo., mt.
23	Sandstone, cherty micaceous	Kutras gravel (Shasta Dam), Calif.	X	6.4	5.0	9.7	Fine	Microq., sericite, quartz, kaolin.	Graphitic matter, limo., mica, chlorite.
24	Sandstone, feldspathic	do	X	4.4	2.4	6.3	do	Microq., feldspar (or., ab.), titanite.	Chlorite; traces leucoxene, limo., hema.
25	do	Cowlitz River gravel, Wash.	Y	4.8	3.5	6.7	Medium	Feldspar 60%, quartz 35%	Mica 3%, chlorite 2%, sericite.
26	do	do	Y	6.8	6.5	8.1	Fine	Microq., feldspar, quartz, sericite, chlorite or antigorite, graphite.	Altered mica; trace of iron oxides.
27	do	Kutras gravel (Shasta Dam), Calif.	X	7.9	7.4	9.1	Medium	Quartz, feldspar, microq	Mica, chlorite, epidote.
28	Chalcedony	Serra do Mar, Brazil		13.8	13.8	14.2	Fine	Fibrous quartz	
29	Flint chat	Lead-zinc mine area, Mo.		11.4	11.8	12.0	Very fine	Microq., chalcedony	Trace of limonite.
30	Chert, brown	Potomac River gravel, Md.-Va.	B	11.2	11.4	11.4	Very fine to fine	Microq. 65%, chalc. 35%	Limonite 1%, trace of quartz.
31	Chert, white	do	B	10.7	10.7	11.0	Very fine	Microq., chalcedony	(Rhombic holes.)
32	Chert, gray	Silver Hill gravel, Md	C	11.3	11.6	11.6	Very fine to fine	Microq. 65%, quartz 35%	
33	Chert, tan	do	C	11.2	11.4	11.6	Very fine	Microcrystalline quartz	Chalcedony, (rhombic holes).
34	Chert, brown	Reading gravel, Mo.	T	11.4	11.6	11.6	Very fine to fine	Microq., quartz	Limonite, (porous).
35	do	do	T	10.9	10.8	11.4	Very fine	do	Limonite.
36	Chert, light gray	Reading gravel, Mo.	T	11.5	11.7	11.9	Very fine	Microq., chalcedony	
37	Chert, brown	do	T	11.8	12.1	12.0	do	Microq., quartz	Limonite, (porous).
38	Chert, white	Tishomingo gravel, Miss.	O	11.0	11.2	11.4	do	Microq., (various shaped holes).	Quartz.
39	Chert, light gray	do	O	11.0	10.9	11.4	do	Microq., chalc., (rhombic holes).	Quartz veinlets.
40	Chert, brown	do	O	11.0	11.0	11.4	Very fine, variable	Microq., (rhombic holes), quartz	Limo., goethite; trace chalc.
41	Chert, light-colored	Bank gravel, Kentucky Dam area, Tenn.	N-1	11.4	11.4	11.9	do	Microcrystalline quartz	(Rhombic holes), quartz.
42	Chert, oolitic	River gravel, Kentucky Dam area, Tenn.	N-2	11.4	11.7	11.8	Very fine to fine, oolitic.	Microq., quartz	Calcite, limonite.
43	Chert, dark gray	Cumberland River gravel, Tenn.	L	11.9	12.4	12.4	Very fine and medium.	Chalc. 65%, microq. 35%	Cal., (rhombic holes): trace limo.
44	Chert, brown	do	L	11.7	11.9	11.9	Very fine	Chalc. 50%, microq. 50%	Limo., (rhombic holes), quartz.
45	do	Estill Springs gravel, Tenn.	M	11.8	12.0	12.3	do	Microcrystalline quartz	(Rhombic holes), limo., quartz.
46	Chert, brown fossiliferous	do	M	11.4	11.8	11.5	Very fine to fine, irregular.	Quartz, microq	Calcite, limonite.
47	do	do	M	11.2	11.3	11.6	do	do	Cal., limo., (rhombic holes)

46	Chert, brown fossiliferous	do	M	11.4	11.8	11.5	Very fine to fine, irregular.	Quartz, microq	Calcite, limonite.
47	do	do	M	11.2	11.3	11.6	do	do	Cal., limo., (rhombic holes).
48	Chert (novaculite)	Camden, Tenn	K	11.4	11.6	11.8	Very fine, even	Microq., (rhombic holes)	Quartz.
49	Chert, calcareous	Quarries in North Central Ohio.	J	10.6	10.8	10.9	Very fine to fine	Microq. 85%, calcite 15%	Trace of iron oxide.
50	do	do	J	11.2	11.5	11.3	do	Microq. 90%, calcite 10%	Quartz; trace of limonite.
51	Chert, calcareous buff	do	J	9.3	9.3	9.4	do	do	Limonite, quartz.
52	Chert, calcareous	Quarry, North, Le Roy, N. Y.	H	11.9	12.6	12.3	do	do	Traces of quartz, graphitic matter.
53	Chert, micaceous	Kutras gravel (Shasta Dam), Calif.	X	7.3	7.2	8.1	Very fine	Microq., sericite	Traces of epidote, actinolite.
54	Opaline chert	San Luis Obispo, Calif		13.4	14.1	14.2	Amorphous	Opal 90%, chalcedony 10%	
55	do	Paso Robles, Calif		13.3	14.6	14.6	do	do	Trace of iron oxide.
56	Opal	Virgin Valley, Nev		6.3	5.8	7.9	do	Opal (relic diatom structures)	
57	Microcline feldspar	Bathurst, Ontario		0.7	0.8	0.9	Single twinned crystal.	Perthite (microcline 90%, ab. 10%).	Quartz less than ½%.
58	Microcline feldspar (measured perpendicular to 010 cleavage face and parallel to *b*-axis).	do		1.1	1.4	1.3	do	Similar to No. 57	
59	Microcline feldspar (measured perpendicular to No. 58).	do		3.5	3.3	3.2	do	Same crystal as No. 58	
60	Microcline feldspar (measured perpendicular to Nos. 58 and 59 and parallel to *a*-axis).	do		17.1	17.3	17.3	do	do	
61	Microcline feldspar	do		2.0	2.5	2.7	do	Similar to Nos. 57 and 58	
62	Oligoclase feldspar	Mitchell Co., N. C		3.1	3.1	3.7	Single crystal	Oligoclase feldspar 99%	Muscovite, quartz.
63	Bytownite feldspar	Unknown		4.2	4.2	4.5	Coarse	Bytownite feldspar 97%	Chlorite, calcite, zeolites.
64	Granite	Potomac River gravel, Md.-Va.	B	9.2	9.3	9.8	Medium	Or., perthite, microcline, quartz, ab.	Garnet, chlorite, limo.
65	do	Port Jefferson gravel, Long Island, N. Y.	D	6.0	5.8	6.8	do	Microcline, quartz, perthite, ab.	Sericite, biotite.
66	do	Bill Williams gravel (Parker Dam), Ariz.	V	1.8	−1.7	4.6	do	Or., microcline, quartz, perthite, ab.	Biotite, sericite.
67	do	Gravel, Kimball, Nebr	U	7.2	6.4	8.4	Medium to coarse	Or., oligoclase, quartz	Musc., zoisite, sericite.
68	Quartz syenite	Lyon Mountain, N. Y	E	7.0	7.3	7.7	Medium	Microcline 45%, perthite 20%, ab. 20%, quartz 10%.	Chlorite, cal., mt., augite, titanite.
69	Augite syenite	do	E	5.3	5.8	6.1	do	Or. and perthite 65%, augite 25%, ab. 5%, mt. 5%.	Quartz, titanite.
70	Granodiorite	Spokane gravel, Irvin, Wash.	Z	3.6	3.7	4.3	do	Pc. 50%, quartz 25%, or. 10%, bio. 5%, hb. 3%.	Titanite, zoisite, chlorite, and sericite, each 2%; traces of mt., apatite, cal.
71	Diorite	do	Z	6.7	6.7	6.7	do	Amphibole (hb. and/or actinolite), pc.	Cal., zoisite, sericite, quartz, mt., titanite.
72	do	Kutras gravel (Shasta Dam), Calif.	X	6.2	5.6	6.9	Medium to coarse	Sericite, oligoclase, hb., chlorite.	Mt., zoisite, epidote, limo.
73	Diorite (altered)	do	X	6.4	6.2	7.4	Medium	Zoisite, hb. and/or actinolite	Quartz, titanite.
74	Diorite (altered)	Kutras gravel (Shasta Dam), Calif.	X	6.6	6.3	7.1	Medium	Zoisite, hornblende, quartz	

See footnotes at end of table.

TABLE 2.—*Description, source, thermal-expansion coefficients, texture, and mineral composition of all materials tested*—Continued.

Specimen number	Description	Source	Designation in table 1	Mean coefficient of linear thermal expansion per degree C×10 [6]			Texture [a]	Mineral constituents [b] (in decreasing order of abundance; percentages approximate only)	
				−20° to +60°	0° to +60°	+60° to 0°		Major, more than 3 percent	Minor, less than 3 percent
75	Monzonite porphyry	Cowlitz River gravel, Wash.	Y	6.7	6.6	7.2	Medium, porphyritic.	Pc., chorite, epidote, sericite	Titanite, calcite.
76	Obsidian	Lake Co., Oreg.		4.5	4.5	4.8	Glassy	Volcanic glass 99%	Feldspar laths.
77	Pitchstone	Magdalena Mts., N. M.		6.8	7.0	7.3	Glassy and fine	Vol. glass 70%, feldspar, quartz 5%.	
78	Trachyte	Cowlitz River gravel, Wash.	Y	5.2	5.0	6.5	Fine, porphyritic	Oligoclase, hb., vol. glass	Magnetite.
79	Trachyte porphyry	Kutras gravel (Shasta Dam), Calif.	X	6.5	6.7	6.4	Fine and medium, porphyritic.	Andesine, chlorite, sericite	Quartz, magnetite.
80	Dacite porphyry	Bill Williams gravel (Parker Dam), Ariz.	V	6.3	6.0	6.7	do	Plagioclase, orthoclase, quartz	Chlorite, hematite, mt.
81	Andesite	do	V	5.8	5.4	6.8	do	Feldspar, sericite, hematite	Volcanic glass (much altered).
82	Andesite porphyry	do	V	7.4	7.4	7.8	do	Lab., vol. glass 25%, bio., augite.	Magnetite.
83	Andesite	Cowlitz River gravel, Wash.	Y	6.2	6.1	6.5	do	Lab., hypersthene (¾ altered to uralite).	
84	do	do	Y	6.4	6.3	6.6	do	Lab., uralite, epidote, augite	Do.
85	Andesite (altered)	do	Y	6.7	6.4	7.5	do	Pc. (much altered), chlorite, sericite, epidote, cal.	Trace of iron oxide.
86	Andesite porphyry	do	Y	3.8	4.1	4.2	Very fine and medium, porphyritic.	Lab., hypersthene, vol. glass	Magnetite.
87	Basalt	Bill Williams gravel (Parker Dam), Ariz.	V	5.7	5.3	6.0	Fine porphyritic	Lab., olivine (¾ altered to iddingsite), augite.	Magnetite, a zeolite.
88	Basalt, vesicular	do	V	4.4	3.7	5.7	do	Lab., olivine (¾ altered to iddingsite.)	Magnetite; trace of calcite.
89	Basalt porphyry	Kutras gravel (Shasta Dam), Calif.	X	6.2	5.9	6.5	Fine and medium, porphyritic.	Labradorite, augite	Magnetite, analcite (?).
90	do	do	X	6.2	6.0	6.6	do	Lab., augite, zoisite	Mt., chlorite, sericite, microq.
91	Basalt	Lyon Mountain, N. Y.	E	6.8	6.9	6.9	Very fine	Plagioclase laths, augite	Chlorite, magnetite.
92	do	do	E	7.0	7.1		do	Same as No. 91	
93	Basalt (diabase)	do	E	7.4	7.3	7.9	Medium	Pc. laths (⅔ altered to sericite), bio., augite, chlorite.	Antigorite (after olivine), mt., apatite, cal., limo.
94	Felsite (altered)	Gravel, Kimball, Nebr.	U	6.1	5.7	6.8	Fine and medium, porphyritic.	Quartz or chalcedonic silica, feldspar.	Biotite, iron oxides.
95	Volcanic breccia	Kutras gravel (Shasta Dam), Calif.	X	6.6	5.6	7.4	Fine and medium	(Small vol. rock fragments); feldspar, vol. glass, quartz, hema., sericite.	Calcite, chlorite.
96	do	Cowlitz River gravel, Wash.	Y	6.9	6.8	7.4	Very fine to fine	(Large vol. rock fragments);	Mt.; traces sericite, calcite.

96	do	Cowlitz River gravel, Wash.	Y	6.9	6.8	7.4	Very fine to fine and very coarse.	(Large vol. rock fragments); pc., epidote, actinolite, chlorite, microq.	Mt.; traces sericite, calcite.
97	do	do	Y	6.1	6.2	8.0	Very fine to medium and coarse.	Pc., quartz, chlorite, microq.	Sericite; traces mt., limo.
98	Phyllite	Buck Dam, Va	A	6.1	0.6	10.7	Very fine	Quartz, microq. and chalc., sericite, calcite.	Micas, limo., feldspar; trace chlorite.
99	do	do	A	6.7	.1	10.7	do	Similar to No. 98	
100	Biotite argillite	Spokane gravel, Irvin, Wash.	Z	9.5	9.6	10.5	Fine	Quartz 45%, sericite 35%, bio. 20%.	Titanite, leucoxene.
101	Sericite argillite	do	Z	9.8	9.8	10.1	do	Quartz 45%, sericite 45%, bio. (part altered to chlorite) 10%.	Musc.; traces py, graphitic matter.
102	Greenstone breccia	Cowlitz River gravel, Wash.	Y	5.1	5.4	5.8	Very fine to fine and coarse.	Actinolite, microq., feldspar (altered).	Titanite, sericite, chlorite, mt.
103	do	Kutras gravel (Shasta Dam), Calif.	X	6.6	6.6	7.5	Fine	Oligoclase, epidote, chlorite, sericite.	Magnetite.
104	do	do	X	8.2	7.3	8.9	Very fine and medium.	Feldspar, chlorite, epidote, sericite.	Quartz.
105	Greenstone	do	X	6.2	6.2	7.0	Fine to medium	Actinolite, quartz, epidote, feldspar.	Titanite, magnetite.
106	Serpentine	do	X	6.0	6.3	6.9	Fine	Antigorite (intersecting lamellas).	Hb. and/or olivine, py., titanite.
107	Chloritic schist	Port Jefferson gravel, Long Island, N. Y.	D	6.7	6.6	7.5	do	Quartz 75%, chlorite 15%, sericite 10%.	Magnetite, feldspar.
108	Calcite (measured parallel to *c*-axis).	Texas, Md		22.5	22.9	23.5	Single crystal	Calcite	
109	Calcite (measured perpendicular to *c*-axis).	do		−4.0	−4.8	−4.2	do	Same crystal as No. 108	
110	Calcite (measured parallel to *c*-axis).	Taos, N. M		25.7	26.3	26.0	Single crystal	Calcite	
111	Calcite (measured perpendicular to *c*-axis).	do		−5.0	−4.8	−4.8	do	Same crystal as No. 110	
112	Limestone	Mille Roche, Canada	I	3.8	4.0	4.1	Fine, variable	Calcite 95%, quartz 4%	Carbonaceous matter, pyrite.
113	do	do	I	4.1	4.3	4.0	Fine to medium, variable.	Similar to No. 112	
114	do	St. Louis Co., Mo	S	3.8	3.9	4.4	Fine to medium, variable.	Calcite, microcrystalline quartz.	Kaolin, quartz; trace py.
115	do	do	S	6.4	5.4	7.4	Fine, variable	Similar to No. 114	
116	Limestone, nodular	Bethany Falls, Mo	R	3.0	3.3	4.3	Very fine	Calcite 98%	Quartz, kaolin, mica.
117	Limestone	Winn Parish, La	P	1.0	0.8	−0.5	Fine to medium	do	Barite.
118	Limestone, banded	do	P	0.9	−.4	−.4	do	Calcite	Traces quartz, limo., carb.
119	Limestone	do	P	6.9	7.7	9.0	Medium to coarse	do	Trace limonite.
120	do	Jordanville, N. Y	G	4.0	4.2	4.4	Medium, variable	do	Quartz; trace carb.
121	do	do	G	4.8	5.0	5.2	do	Similar to No. 120	
122	do	do	G	9.1	9.7	9.9	do	do	
123	do	North Le Roy, N. Y	H	5.6	5.7	5.8	Fine	Calcite 99%	Traces carb., kaolin, quartz.
124	do	do	H	4.4	4.9	4.9	do	Similar to No. 123	
125	Limestone, sandy	Gravel, Kimball, Nebr	U	3.6	3.5	4.6	Fine to medium	Calcite 50%, quartz, feldspar	Opal, mica.
126	Limestone, siliceous	Spokane gravel, Irvin, Wash.	Z	9.8	10.1	10.2	Very fine	Calcite, quartz	Musc., limo., pyrite.

See footnotes at end of table.

TABLE 2.—*Description, source, thermal-expansion coefficients, texture, and mineral composition of all materials tested*—Continued

Specimen number	Description	Source	Designation in table 1	Mean coefficient of linear thermal expansion per degree C x10 [6]			Texture [a]	Mineral constituents [b] (in decreasing order of abundance; percentages approximate only)	
				−20° to +60°	0° to +60°	+60° to 0°		Major, more than 3 percent	Minor, less than 3 percent
127	Limestone, siliceous dolomitic (measured parallel to bedding planes).	Paso Robles, Calif.	W	8.6	9.1	9.4	do	Dolomite and cal., opal 10%, chalc. 10%.	
128	Limestone, siliceous dolomitic (measured perpendicular to bedding planes).	do	W	9.4	9.7	10.0	do	Same as No. 127	
129	Limestone, siliceous dolomitic (measured parallel to bedding planes).	do	W	8.9	9.2	9.3	do	Similar to No. 127	
130	Limestone, siliceous dolomitic (measured perpendicular to bedding planes).	do	W	9.5	9.8	9.8	do	Same as No. 129	
131	Dolomite	Norwood, N. Y.	F	6.6	5.9	8.1	Fine	Dolomite 95%, quartz 5%	Carbonaceous matter.
132	do	do	F	7.6	7.7	8.3	do	Similar to No. 131	
133	do	Elgin gravel, Ill.	Q	8.2	8.6	8.7	do	Dolomite	Quartz.
134	do	do	Q	7.3	7.1	8.4	do	do	Limonite.
135	do	do	Q	7.2	7.6	8.9	do	Dolomite, quartz 5%	
136	Dolomite, limonitic sandy	do	Q	8.7	8.5	9.3	do	Dolomite 50%, quartz 50%	Musc., limo., feldspar.
137	Magnesite	Muntodi, Greece	----	8.1	7.5	9.2	Very fine	Magnesite, kaolin 5%	Trace limonite.

[a] Grain size terminology designates the following approximations in millimeters:

Very fine-grained	Less than 0.02.
Fine-grained	0.02 to 0.2.
Medium-grained	0.2 to 2.0.
Coarse-grained	2.0 to 10.0.
Very coarse-grained	Over 10.0.

[b] Abbreviations used:

ab	albite.	limo	limonite.
bio	biotite.	microq	microcrystalline quartz.
cal	calcite.	musc	muscovite.
carb	carbonaceous matter.	mt	magnetite.
chalc	chalcedony.	or	orthoclase feldspar.
hb	hornblende.	pc	plagioclase feldspar.
hema	hematite.	py	pyrite.
lab	labradorite.	vol	volcanic.

V. RESULTS AND DISCUSSION

The coefficients of linear thermal expansion of all materials tested are given for three different temperature ranges in table 2. Typical expansion curves of some of the materials are shown in figures 3 to 10, inclusive. Variations in these coefficients for similar rocks or minerals may be attributed to three main factors, namely, crystal orientation, composition difference, and texture.

1. EFFECT OF CRYSTAL ORIENTATION

Measurements were made on oriented crystals of calcite (fig. 3), quartz (fig. 4), and microcline feldspar (fig. 5) to illustrate the differences in thermal expansivity that occur in minerals along different crystallographic axes. These values are given in table 3, together with values reported by other investigators. It can be seen, therefore, that with such minerals the thermal-expansion measurements on individual crystals of unknown orientation are of limited value.

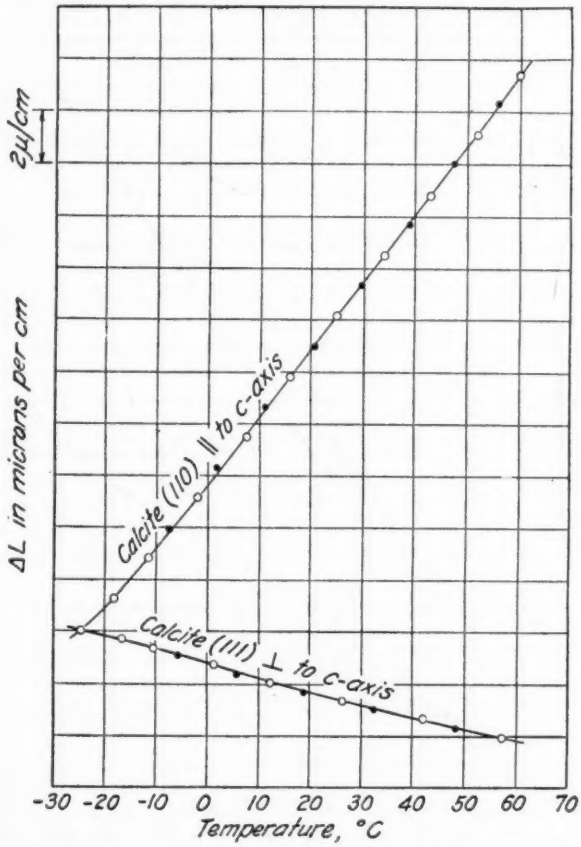

FIGURE 3.—*Thermal-expansion curves of a crystal of calcite in two crystallographic directions.*

○ Are heating points; ● are cooling points. Figures in parentheses refer to the specimen numbers in table 2.

TABLE 3.—*Mean coefficients of linear thermal expansion for oriented mineral specimens*

Specimen number	Mineral	Orientation	Temperature interval	Mean coefficient of linear thermal expansion per °C×10⁶	Investigator
			°C		
1	Quartz	Perpendicular to *c*-axis	0 to 60	14.0	Johnson and Parsons.
2	do	Parallel to *c*-axis	0 to 60	7.7	Do.
	do	Parallel to *c*-axis	0 to 100	8.0	Sosman [14].
	do	Perpendicular to *c*-axis	0 to 100	14.4	Do.
58	Microcline	Perpendicular to 010 cleavage; parallel to *b*-axis.	0 to 60	1.4	Johnson and Parsons.
59	do	Perpendicular to specimen 58	0 to 60	3.3	Do.
60	do	Perpendicular to specimens 58 and 59; parallel to *a*-axis.	0 to 60	17.3	Do.
	Orthoclase *	Parallel to *b*-axis	20 to 100	0.0	Kozu and Saiki [15].
	do *	Parallel to *a*-axis	20 to 100	15.0	Do.
110	Calcite	Parallel to *c*-axis	18 to 50	26.3	Johnson and Parsons.
111	do	Perpendicular to *c*-axis	18 to 50	−4.8	Do.
	do	Parallel to *c*-axis	18 to 50	25.1	Austin and coworkers [16]
	do	Perpendicular to *c*-axis	18 to 50	−4.9	Do.

* As no data regarding the thermal expansion of microcline are found in the literature, published coefficients for orthoclase are given for comparison with microcline. Both minerals are $KAlSi_3O_8$, but vary slightly in certain crystallographic and optical properties.

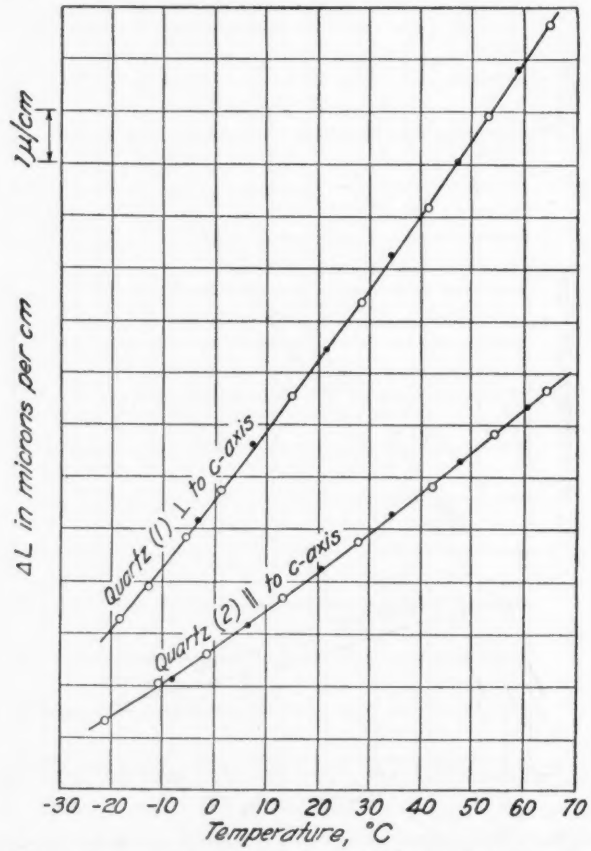

FIGURE 4.—*Thermal-expansion curves of a crystal of quartz in two crystallographic directions.*

○ Are heating points; ● are cooling points. Figures in parentheses refer to the specimen numbers in table 2.

This is illustrated by specimen 62 (table 2), oligoclase feldspar, which shows a coefficient of 3.1×10^{-6} per degree centigrade but whose orientation is unknown.

A monomineralic rock composed of many crystals with haphazard crystallographic orientations should have, in all directions, a thermal-expansion coefficient representing an average of all possible orientations of the mineral concerned. The 19 cherts, for example, which are composed almost entirely of very fine-grained quartz (specimens 30 to 48, table 2) all have nearly equal thermal-expansion coefficients, averaging 11.3×10^{-6} per degree centrigrade. This value is very close to the arithmetric average of the thermal expansion of quartz in all crystallographic directions, and, therefore, is representative of the coefficient of thermal expansion of rocks composed almost entirely of quartz grains with random orientations. If, on the other hand, a rock has more of its component crystal grains oriented in one direction than in any other, the coefficient of expansion in that direction will be different from those in other directions. An example of this is the siliceous dolomitic limestone from Paso Robles, Calif. (specimens 127 to 130,

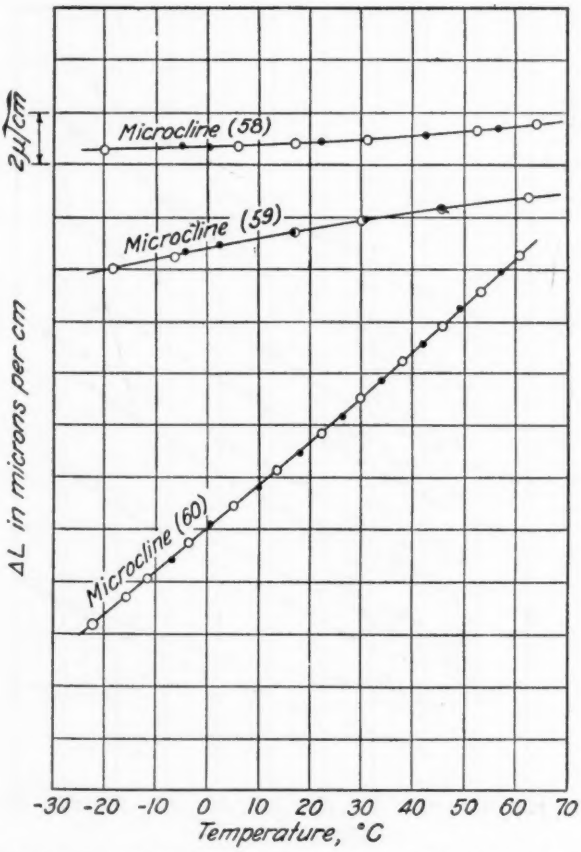

FIGURE 5.—*Thermal-expansion curves of a crystal of microcline feldspar.*

No. 58 perpendicular to 010 cleavage face and parallel to *b*-axis; No. 59, perpendicular to No. 58; No. 60, perpendicular to Nos. 58 and 59 and parallel to *a*-axis. ○ Are heating points; ● are cooling points; figures in parentheses refer to specimen numbers in table 2.

table 2), which has a coefficient of 8.7×10^{-6} parallel to its bedding planes and 9.4×10^{-6} perpendicular to its bedding planes. Another suspected example is the limestone from Jordanville, N. Y. Three specimens of this limestone taken in random directions gave coefficients of 4.0, 4.8, and 9.1×10^{-6} (Nos. 120, 121, and 122).

2. EFFECT OF COMPOSITION DIFFERENCE

Rocks from various sources but of similar composition have approximately the same expansivities, if orientation differences are disregarded. This is true for the siliceous rocks (fig. 6), the calcitic limestones (fig. 7), and the dolomites (fig. 7). As a specific example, cherts 30 to 48 (table 2), which were composed of little but silica, had notably similar coefficients ranging from 10.7 to 11.9×10^{-6}. When other minerals were present, however, as in Nos. 49 to 53, which contained varying amounts of calcite and mica (sericite), the coefficients ranged from 7.3 to 11.9×10^{-6}. Compare also sandstones 16 and 22 (fig. 8) and limestones 112 and 129 (fig. 8).

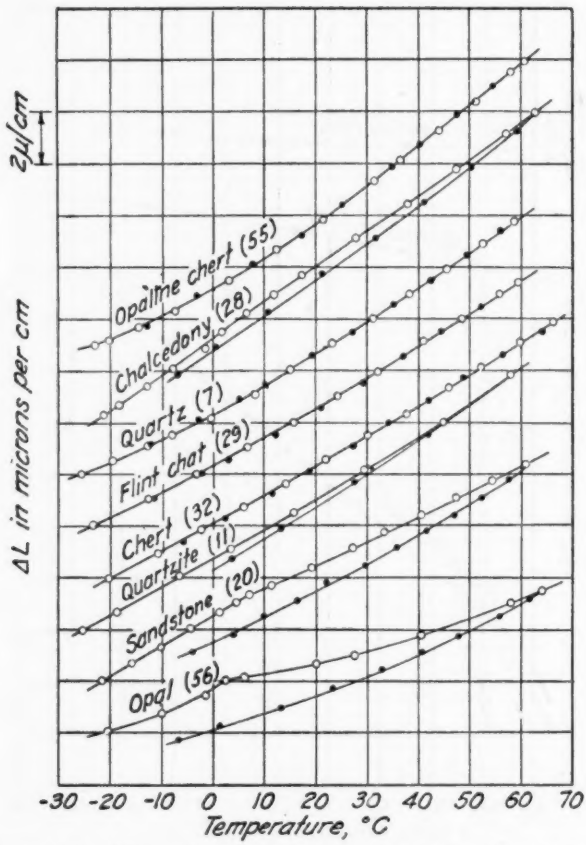

FIGURE 6.—*Thermal-expansion curves of various siliceous rocks.*

○ are heating points; ● are cooling points. Figures in parentheses refer to the specimen numbers in table 2.

3. EFFECT OF TEXTURE

The kind of texture here considered is grain size, although other textures, such as crystallinity or noncrystallinity, may have important effects on rock expansivities. The grain size is particularly important in the present method of test because of the small size of the test specimen. The average height of the latter was only about 0.25 in., and the expansion of only one spacer was measured. The total number of grains through which measurement was made is strictly a function of the grain size of the rock and, based on the terminology given in section IV, was estimated to be as follows:

For very fine-grained rocks	More than 300.
For fine-grained rocks	30 to 300.
For medium-grained rocks	3 to 30.
For coarse-grained rocks	1 to 3.
For very coarse-grained rocks	Less than 1.

The thermal-expansion coefficient of a specimen of very fine-grained, randomly oriented rock is, therefore, an average of all possible crystal

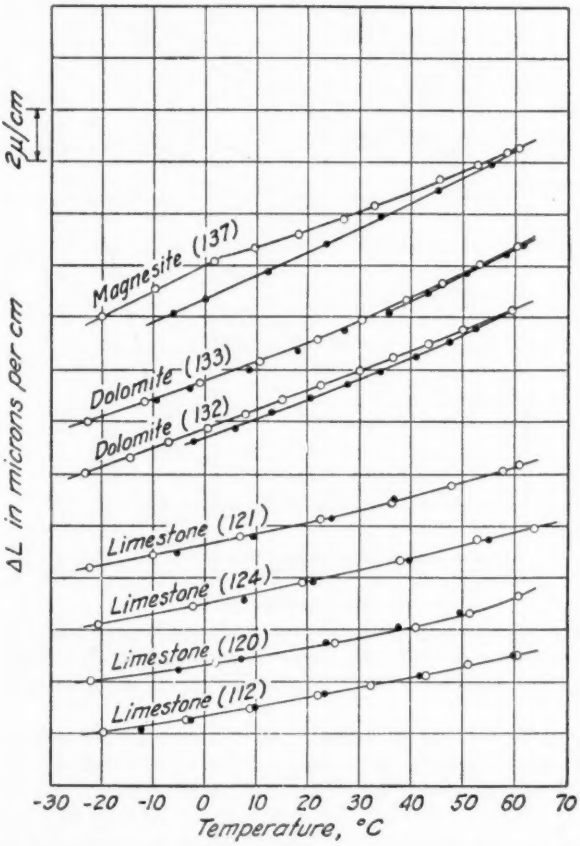

FIGURE 7.—*Thermal-expansion curves of various carbonate rocks.*

○ Are heating points; ● are cooling points. Figures in parentheses refer to specimen numbers in table 2.

orientations of all minerals in that rock and represents the actual expansivity of the rock. The coefficient given for a coarse-grained rock, however, may actually represent the expansivity of only one crystal orientation of one mineral and accordingly, cannot be considered as a true representation of the expansivity of that entire rock.

In the igneous and volcanic rocks, which have several minerals as part of their essential compositions and a large number of possible accessory and alteration minerals, considerable variation in expansivity

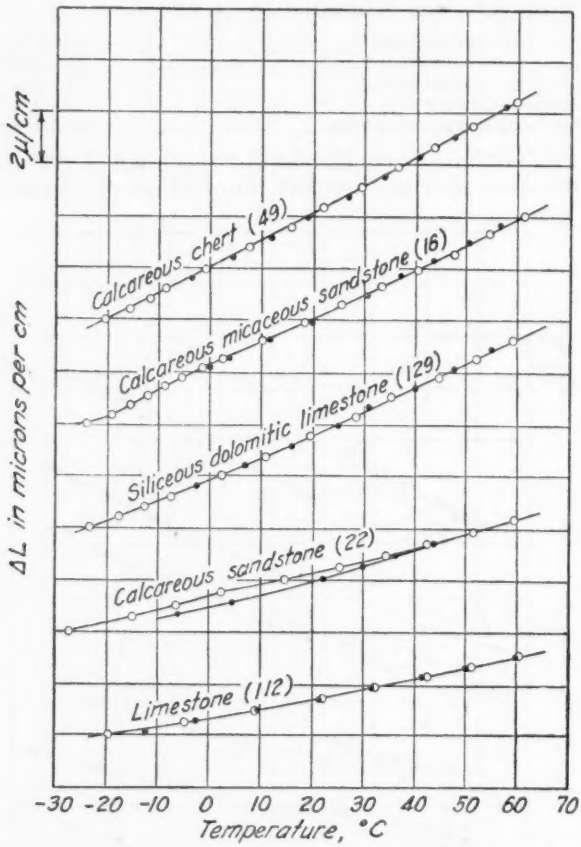

FIGURE 8.—*Thermal-expansion curves of rocks containing varying amounts of calcite compared with a pure calcite limestone* (No. 112).

○ Are heating points; ● are cooling points. Figures in parentheses refer to the specimen numbers in table 2.

is to be expected. This is noted in the four granites (specimens 64 to 67, table 2) whose coefficients range from 1.8 to 9.2×10^{-6}, and to a lesser extent in the andesites (Nos. 81 to 86) and basalts (Nos. 87 to 93). The group average for the expansivity of any one of these rock types is not a very significant figure, since the composition of such rocks is not necessarily as constant as the name suggests.

Also, different specimens of a particular mineral may differ in composition; for example, the combined water in opal varies in diff-

erent opal specimens. This may help to explain the expansivity differences (table 2 and fig. 6) between Nevada opal (No. 56, coefficient 6.3×10^{-6}) and California opaline chert (specimens 54 to 55, coefficients 13.4 and 13.3×10^{-6}).[2]

4. MATERIALS WITH IRREGULAR EXPANSION

Some materials do not expand uniformly on heating and the resulting expansion curves show more or less definite breaks in their con-

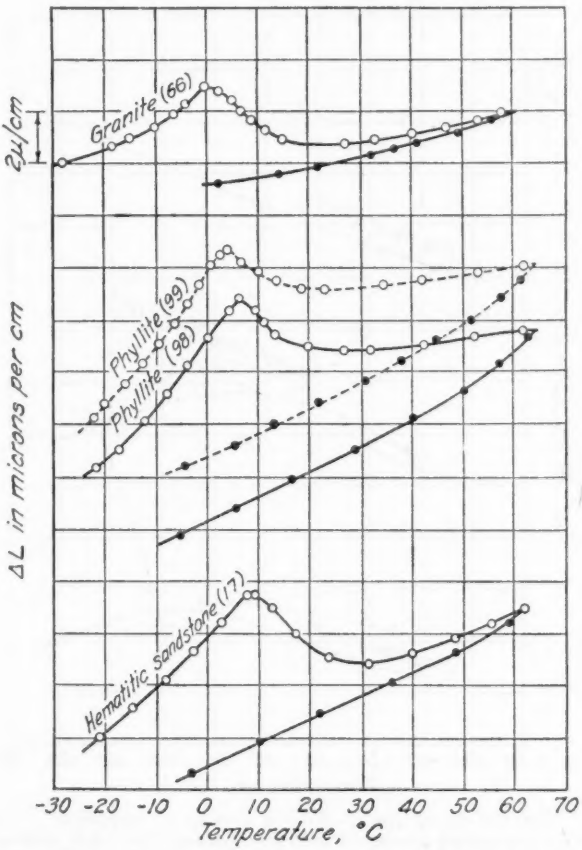

FIGURE 9.—*Thermal-expansion curves of rocks with irregular expansion.*

Nos. 98 and 99 are different specimens of the same rock sample; No. 66 was measured twice and No. 17 four times, and identical curves, respectively, were obtained each time: ○ are heating points; ● are cooling points. Figures in parentheses identify specimens in table 2.

tinuity because of a change in the rate or a change in the direction of expansion. In most of these cases the materials expand on heating until temperatures between 0° and 10° C have been reached. With further heating they either expand at a lesser rate (opal, No. 56, and sandstone 20, fig. 6) or contract (fig. 9) until temperatures between 15° and 30° C have been reached, when expansion is resumed. As a

[2] Nevada opal showed an ignition loss at 1,300° C of 5.4 percent and the opal of the California opaline chert an ignition loss of 7.3 percent.

general rule, these irregularities are not evident on cooling. Two specimens of a Louisiana limestone, however, were found that exhibited reversals both on heating and on cooling (fig. 10). The specimens exhibiting irregular expansion were retested with similar results; for example, specimen 66 (fig. 9) was measured by both the visual and the photographic methods, and specimen 17 (fig. 9) was tested twice by both methods. Identical curves were obtained, respec-

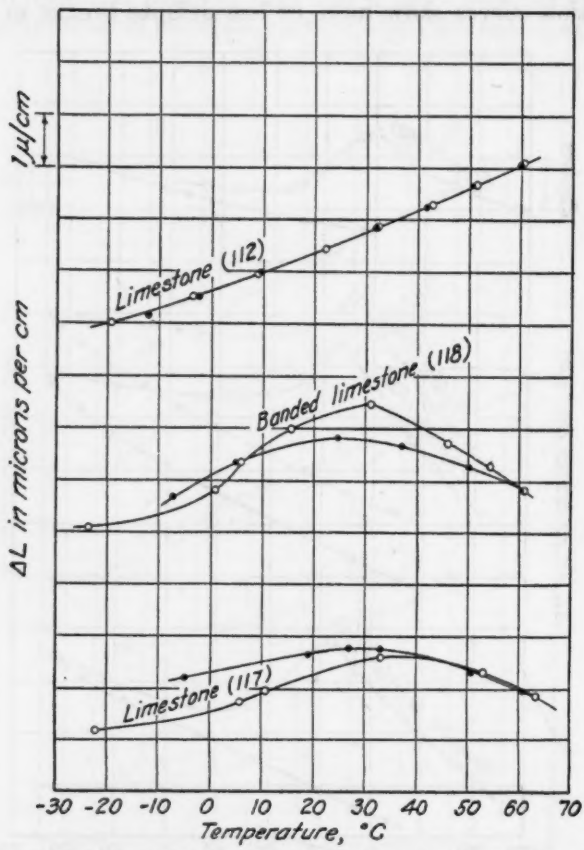

FIGURE 10.—*Thermal-expansion curves of a limestone (specimens No. 117 and 118) with irregular expansion compared with a limestone (No. 112) with regular expansion.*

○ are heating points; ● are cooling points. Figures in parentheses identify the specimens in table 2.

tively, for both specimens when retested. The coefficients given in table 2 inadequately describe the thermal-expansion behavior of these materials. For this reason, table 4 has been prepared to give the average thermal coefficients between those points where sudden changes in rates of expansion occurred.

It is possible that these irregularities are caused by capillary water in the specimens. The specimens were dried for several days over $CaCl_2$, but all water was not necessarily removed. The specimens were held overnight at temperatures well below freezing, so that some

of the capillary water present was undoubtedly frozen. As the ice melted, two complicating factors affected the rate of expansion of the specimens, namely (1) the volume change occurring as ice melts into the corresponding smaller volume of water, and (2) the change in heating rate of the specimen as the heat of crystallization of the water is absorbed. The latter factor may help to explain the occurrence of the breaks in continuity a few degrees above 0°C. Additional

TABLE 4.—*Mean coefficients of linear thermal expansion, between points of inflection, of materials having irregular expansions*

Specimen number	Material	Temperature interval	Mean coefficient of linear thermal expansion per ° C×10⁶	Specimen number	Material	Temperature interval	Mean coefficient of linear thermal expansion per ° C×10⁶
		° C				° C	
17	Hematitic sandstone	−20 to 8	18.8	98	Phyllite	−20 to 7	23.4
17	do	8 to 30	−12.9	98	do	7 to 30	−8.4
17	do	30 to 60	6.4	98	do	30 to 60	2.4
19	Limonitic sandstone	−20 to 6	13.6	99	do	−20 to 4	24.8
19	do	6 to 17	−4.0	99	do	4 to 23	−8.0
19	do	17 to 60	9.2	99	do	23 to 60	3.3
21	Argillaceous sandstone	−20 to 15	10.5	115	Limestone	−20 to 4	9.2
21	do	15 to 60	3.2	115	do	4 to 20	2.1
				115	do	20 to 60	6.4
24	Feldspathic sandstone	−20 to 6	9.7				
24	do	6 to 26	−3.4	117	do	−20 to 35	2.3
24	do	26 to 60	4.9	117	do	35 to 60	−2.3
				117	do	60 to 30	−2.7
25	do	−20 to 6	9.5	117	do	30 to 0	1.6
25	do	6 to 18	−2.2				
25	do	18 to 60	3.9	118	do	−20 to 31	4.5
				118	do	31 to 60	−5.4
26	Opal	−20 to 2	8.5	118	do	60 to 25	−2.8
26	do	2 to 60	5.4	118	do	25 to 0	3.0
86	Granite	−20 to −1	12.5	119	do	−20 to 25	3.9
86	do	−1 to 22	−10.6	119	do	25 to 60	10.7
86	do	22 to 60	3.2				
				131	Dolomite	−20 to 4	8.2
87	do	−20 to 4	10.5	131	do	4 to 7	−1.1
87	do	4 to 15	−1.5	131	do	7 to 60	6.7
87	do	15 to 60	8.0				
				134	do	−20 to 6	7.5
96	Volcanic breccia	−20 to 7	10.1	134	do	6 to 11	−1.8
96	do	7 to 60	4.7	134	do	11 to 60	8.2
97	do	−20 to 13	5.7				
97	do	13 to 15	−4.0				
97	do	15 to 60	7.0				

study is needed on the effects of capillary water in the various materials. The irregular expansion of the limestone from Winn Parish, La., (specimens 117 and 118, table 4 and fig. 10) does not seem explainable as a water phenomenon, but no other explanation for these curves has yet been suggested.

5. COMPARISON OF PRESENT RESULTS WITH PREVIOUS WORK

The average coefficients for groups of similar rocks, as determined in the present study, are compared in table 5 with the results of other recent investigations. Not only are there variations in the average coefficients reported by the several investigators, but there are also considerable differences in values for individual specimens of the same

rock type as determined in the present investigation (see range of coefficients, table 5). Although most of the average values obtained by other investigators differ from the averages given in the present paper, they do fall within or close to the range of values obtained for individual specimens in this study. The lack of agreement may be due to differences in methods of investigations, in temperature ranges, in crystal orientations, and in mineral composition and textures of the rocks used by the various investigators.

TABLE 5.—*Mean coefficients of linear thermal expansion of similar materials determined by other investigators and compared with the results of the present study*

Material	Number of specimens	Temperature range	Mean coefficients of linear thermal expansion per °C × 10^6		Investigator
			Average	Range	
		°C			
Quartzite	9	−20 to+60	9.9	7.0 to 12.2	Johnson and Parsons.
Do	3	20 to 100	10.6		Griffith [4].
Do	5	0 to 60	11.7		Willis and De Reus [5].
Sandstone	11	−20 to+60	7.4	4.4 to 10.4	Johnson and Parsons.
Do	10	20 to 100	9.8		Griffith [4].
Do	[a] 5	0 to 60	11.7		Willis and De Reus [5].
Chert	24	−20 to+60	11.1	7.3 to 11.9	Johnson and Parsons.
Do	1	20 to 100	11.5		Griffith [4].
Do	22	0 to 60	12.2		Willis and De Reus [5].
Granite	4	−20 to+60	6.1	1.8 to 9.2	Johnson and Parsons.
Do	17	20 to 100	7.9		Griffith [4].
Do	2	0 to 60	5.5		Willis and De Reus [5].
Other granitic rocks: syenite, diorite, monzonite.	8	−20 to+60	6.1	3.6 to 7.0	Johnson and Parsons.
Basalt	7	−20 to+60	6.2	4.4 to 7.4	Do.
Do	4	20 to 100	4.8		Griffith [4].
Do	2	0 to 60	9.4		Willis and De Reus [5].
Other felsitic rocks: andesite, dacite, trachyte.	10	−20 to+60	6.0	3.8 to 7.4	Johnson and Parsons.
Limestone	13	−20 to+60	4.4	0.9 to 9.1	Do.
Do	22	20 to 100	7.9		Griffith [4].
Do	5	0 to 20	4.6		Do.
Do	16	0 to 60	4.6		Willis and De Reus [5].
Do	5	−7 to+88	7.6		Koenitzer [6].
Marble [b]	2	−32 to+24	1.2		Pearson [1].
Do. [b]	2	24 to 100	7.8		Do.
Do	9	24 to 100	11.3		Souder and Hidnert [7].
Siliceous limestone	6	−20 to+60	8.3	3.6 to 9.8	Johnson and Parsons.
Dolomite	6	−20 to+60	7.6	6.6 to 8.7	Do.
Dolomitic marble	1	−17 to+49	3.6		Pearson [1].

[a] Measurements made on water-saturated specimens.
[b] Same specimens.

6. AGGREGATE EXPANSIVITY IN RELATION TO CONCRETE

The coefficient of linear thermal expansion of hardened portland cement varies considerably with such factors as the kind and composition of the cement, the water-cement ratio, and the age [8]. This coefficient varies within the normal range of atmospheric temperatures between limits of approximately 11×10^{-6} and 16×10^{-6} per degree centigrade (6 and 9×10^{-6} per degree Fahrenheit), according to Davis [8], Pearson [1], and others [9]. As pointed out in the introduction, large differences in coefficients between the cementitious

material and the aggregate may lead to concrete failure where severe weather conditions are encountered.

The discussion in section V, 1 to 4, indicates four types of materials, classified according to expansivity characteristics, which might manifest themselves unfavorably in concrete. These are (a) materials having a uniform coefficient of thermal expansion markedly different from the normal value for concrete; (b) an aggregate composed of single crystal fragments with different expansivity in various crystallographic directions; (c) an aggregate (a gravel or a crushed coarse-grained rock) composed of two or more fractions which are present in considerable amounts and have widely different expansivities; and (d) a material with irregular expansion of the type illustrated in figures 9 and 10. At least two instances of disintegration of concrete have been ascribed recently to type (a), namely: a dolomitic marble aggregate with a thermal coefficient of 3.6×10^{-6} per degree centigrade studied by Pearson [1] and a fine-grained limestone aggregate with a coefficient of 4.0×10^{-6} per degree centigrade mentioned by Hornibrook [2]. These aggregates were used in concretes that disintegrated after exposure to one northern United States winter. An example of (b) has been pointed out in Central New York by Swayze [17], where a coarse aggregate consisting of single calcite crystals was used in a cast stone. This stone was in very bad condition after exposure to one winter. The Kimball, Nebr. gravel is a possible example of (c). This gravel contains about 90 percent of granite with a thermal-expansion coefficient of 7.2×10^{-6} (specimen 67, table 2). About half of the granite, however, is broken into fragments of quartz and orthoclase feldspar, minerals whose thermal-expansion coefficients vary with crystallographic directions between limits of 8.0 and 14.4×10^{-6} [14] and of 0.0 and 15.0×10^{-6} [15], respectively.

Most of the aggregate materials listed in table 2, excluding single crystals, have thermal expansions close to or within the range of expansions for hardened portland cement. A few, however, have sufficiently different expansivities to warrant some question as to their satisfactory use under severe weather conditions. Where aggregates containing such materials in large amounts are to be used in severe exposures, an examination should be made of the service record in structures having similar exposures. Lacking service background, they should be subjected to laboratory tests of the type described by Pearson [3].

VI. SUMMARY

Descriptions are given of an apparatus and test procedure used to measure the linear thermal expansion of 137 specimens of rocks and minerals found in concrete aggregates. The mineral constituents and textures of these specimens were determined petrographically. The common aggregate materials, excluding single crystals, were found to have thermal-expansion coefficients ranging from 0.9 to 13.8×10^{-6} per degree centigrade within the range of $-20°$ to $+60°$ C ($-4°$ to $+140°$ F). The majority of the coefficients are close to the coefficients of hardened portland cement. Crystal orientation, composition differences, and texture are factors which cause variations in the thermal expansions of aggregate materials. Some rocks do not expand uniformly on heating. Under severe weather conditions, the

expansivity of an aggregate might manifest itself unfavorably in concrete containing one of the following aggregate types: An aggregate having a uniform thermal expansion markedly different from the normal expansion of concrete; an aggregate composed of large crystal fragments having different thermal expansion in different crystallographic directions; an aggregate composed of two or more fractions with widely different expansivities; or an aggregate with irregular expansion.

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SCALE SUBSTANCE OF WOOL

By Walton B. Geiger [1]

ABSTRACT

Earlier work at this Bureau has shown that wool that has been reduced with thioglycolic acid and then alkylated with ethyl bromide is attacked by pepsin in such a way that the scale material remains intact, whereas the interior of the fiber is completely dissolved. The composition of the scale material so obtained has now been studied. It has been found that it is essentially protein in chemical nature and, although it contains the same amino acids as the whole wool, the proportions of these in the two materials differ; thus, the whole wool used in this work contained 12.2 percent of cystine, 8.6 of arginine, 6.1 of tyrosine, and 9.5 of serine, whereas the scale material contained 20.3, 4.8, 3.3, and 11.2 percent, respectively.

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I. INTRODUCTION

A wool fiber usually consists of three concentric regions: (1) a thin outer layer called the cuticle, usually about 1 to 2 microns thick and made up of overlapping scales, (2) the cortex, or main body, of the fiber, and (3) a central pith, or medulla [1].[2] In fine wool, the last is generally lacking. The cuticle has been suggested to have a protective function, since it is mechanically tougher and chemically more stable than the rest of the fiber [1, 2, 3, 4]. It has been suggested also that the ability of wool fibers to felt is at least partially dependent on these scales (literature reviewed in [5]).

Little is known about the composition of the scales, since ready means for separating them from the rest of the fiber have not been available. From experiments involving partial hydrolysis of wool with hydrochloric acid, Trotman, Trotman, and Sutton [4] concluded that the scales were richer in sulfur than the cortex. Also, a number of investigators [6, 7, 8, 9] have concluded from color tests made under the microscope that the cuticle contains little or no tyrosine.

Recent work at this Bureau [10] has shown that wools chemically modified by reduction with thioglycolic acid, followed by alkylation

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[2] Figures in brackets indicate the literature references at the end of this paper.

with methyl iodide or ethyl bromide, are attacked by pepsin, and that the pepsin digests the inner portions of the fiber, leaving the cuticle intact. The present paper reports some analytical results on the composition of scale material obtained in this way.

II. EXPERIMENTAL PROCEDURE

1. REDUCTION AND ALKYLATION

The reduction and alkylation were carried out by methods similar to those previously described [11, 12]. A 140-g sample of wool was reduced for 24 hr at 35° C with 4,000 ml of a 0.2 *N* solution of sodium thioglycolate brought to pH 8.0 with potassium hydroxide. The yarn was then removed from the solution, washed thoroughly with water, and alkylated by treating it for 2 hr with 2,000 ml of a 0.1 *N* phosphate buffer solution at pH 8.0, in which had been suspended 25 g of ethyl bromide. After again washing the wool with water, the processes of reduction and alkylation were repeated. The product was again washed, dried, and finally comminuted in a Wiley mill.

2. TREATMENT WITH PEPSIN

The chemically modified wool was suspended in 3,000 ml of a 0.2 *M* solution of potassium chloride, which was adjusted to pH 1.1 by the addition of hydrochloric acid, and which contained 1.0 g of pepsin.[3] The suspension was kept at 35° C and slowly stirred for 5 days. After this length of time, examination under the microscope indicated that the residue consisted almost entirely of scales, and that all the cortical material had been dissolved.

The scale material was separated by centrifuging and was washed several times with a 5-percent solution of potassium chloride and several times with distilled water. The material then was dried by washing it with alcohol and then with ether, and the final drying was done over concentrated sulfuric acid in a vacuum desiccator. The dried product formed a light-brown, horny mass weighing 3.283 g, representing about 2.3 percent of the weight of the wool.

III. RESULTS AND DISCUSSION

Preliminary qualitative tests of the scale material indicated that it was composed largely of protein. It gave positive xanthroproteic [13] and biuret [13] reactions. Moreover, the Millon [13] reaction, given by proteins containing tyrosine or tryptophane, the alkali-plumbite [14] reaction, given by those containing sulfur, and the Sakaguchi [13] reaction, given by those containing arginine, were all positive. The Ehrlich [13] reaction for amino sugars was negative. Only a faintly positive test for carbohydrate was obtained when the Molisch [13] test was applied. No carbohydrate could be detected by using Fehling's solution or by Beek's [15] method. A test for bound lipid by the method of Anderson [16] showed that the material contained 2.7 percent of lipid. On ignition [17], 4.13 percent of ash was found to be present.

Determination of nitrogen by the micro-Kjeldahl procedure of Clarke [18] gave 13.53 percent, somewhat less than the amount usually

[3] From Fairchild Bros. & Foster, New York, N. Y.

found in proteins, but correction for ash, lipid, and the ethyl groups introduced chemically increased this to 15.17 percent, a value just slightly lower than that given by wool (table 1). This difference seems largely due to the smaller arginine content of the scale material, which contained only about half as much arginine (4.8 percent) as whole wool (8.6 percent). Arginine is the richest in nitrogen of the amino acids. The scale material contained 5.42 percent of sulfur [20], which is considerably more than that in untreated wool (3.50 percent).

TABLE 1.—*Composition of untreated wool and of wool scales*

Constituent	Untreated wool	Wool scales	
		Found	Corrected value [a]
Sulfur	3.50	4.83	5.42
Cystine	12.2	[b]18.1	[b]20.3
Nitrogen	16.67	13.53	15.17
Arginine	8.6	4.3	4.8
Tyrosine	6.1	3.0	3.3
Serine	9.5	9.9	11.2
Ethyl groups	0.0	4.0	----------
Ash	.2	4.1	----------
Lipid	----------	2.7	----------

[a] Corrected for the presence of ethyl groups, ash, and bound lipid, as described in the text.
[b] Calculated from the sulfur content.

The sulfur in the scale material probably was largely in the form of S-ethyl cysteine, since the determination of the ethyl groups [21] showed that 4.0 percent was present, a result which indicates that 1.51 millimoles of sulfur and 1.38 millimoles of ethyl groups were present per gram of scale material. This S-ethyl cysteine had doubtless been formed from cystine by the reduction and alkylation processes used in preparing the material.

Determination of the tyrosine in the scale material [22] showed that it contained only about half as much (2.97 percent) as wool (6.10 percent). Analysis by the method of Nicolet and Shinn [23] showed that the scale material contained about the same amount of serine as wool.

IV. CONCLUSIONS

Analytical studies of the cuticle of wool and of whole wool fibers show that although both contain the same amino acids, the proportions of these in the two materials differ. The presence of larger amounts of sulfur presumably means that the protein of the scales contains more sulfur cross-links between its peptide chains than do the more digestible proteins of the cortex. Nevertheless, even when the sulfur cross-links have been broken as in the present product, the material is not digested by enzymes. Moreover, the scale material was found to be more stable toward alkali than wool that had been reduced and alkylated in the same way, since the alkali-solubility [24] of the scale material was found to be only 42 percent and that of the treated wool 85 percent.

Two possible explanations have been advanced to account for the difference in behavior of the cuticle and the cortex of wool. Speakman, and also Rudall, have suggested that, since the cortex of wool

fibers is attacked more rapidly by sodium sulfide than are the scales, cross-links other than those involving sulfur may be present. This hypothesis is supported by the results of the present work, although direct proof of the existence and nature of such cross-links is still lacking. An alternative explanation might be sought in the recent demonstration by Hock and McMurdie [25], with the electronmicroscope, that the cuticle and cortex differ widely in physical organization.

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